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β-Barium Borate Thin Film Formation on Silicon Through Metal Organic Decomposition of Two Novel Precursors, Barium Dimesitylborinate and Barium (18-Crown-6) Cyclotriboroxane

Timothy M. Gross

Thesis

Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Science

Approved:

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June, 2004

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LIST OF ABBREVIATIONS

BBO	Barium Borate
CE	Crown Ether (18-crown-6)
DSC	Differential Scanning Calorimetry
IR	Infrared
KDP	Potassium Dihydrogen Phosphate
MOCVD	Metal Organic Chemical Vapor Deposition
MOD	Metal Organic Decomposition
NLO	Non-Linear Optical
NMR	Nuclear Magnetic Resonance
RCA	Radio Corporation of America
SHG	Second Harmonic Generation
TGA	Thermal Gravimetric Analysis
TLC	Thin Layer Chromatography
UV	Ultra Violet
XRD	X-Ray Diffraction

ELLIPSOMETRY ABBREVIATIONS

NF	Refractive Index of Film
NS	Refractive Index of Substrate
CD	Calculate Thickness of Film Command
CNDE	Calculate the Index of Refraction and Thickness Command
CNS	Calculate the Index of Refraction of the Substrate Command

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ABSTRACT

Two novel precursors, barium dimesitylborinate and barium (18-crown-6) cyclotriboroxane, were synthesized to produce thin films of β–barium borate (β–$Ba_3B_6O_{12}$) via the metal organic decomposition (MOD) process.

The two precursor reagents were characterized by nuclear magnetic resonance, infrared spectroscopy, differential thermal analysis (DSC), thermal gravimetric analysis (TGA), and elemental analysis. The MOD process was initially used to produce β–barium borate powders. The powders were heated for 1 hour under oxygen flow at various temperatures. The formation of β–barium borate was confirmed by powder X-ray diffraction of the products of thermolysis of both precursors. β–barium borate formation occurred at 800 °C and 550 °C for barium dimesitylborinate and barium (crown ether) cyclotriboroxane, respectively.

Thin films of both precursor compounds were produced by a spin coating process. The substrates used were silicon wafers with a (100) orientation. Tetrahydrofuran was found to be a good solvent for the barium dimesitylborinate precursor. Ethanol was used for barium (crown ether) cyclotriboroxane. Again, the MOD process was used. The films were heated to various temperatures for various times under flowing oxygen. The films were then analyzed by thin film X-ray diffraction to determine if β–barium borate was formed. Due to substrate interaction thin films produced from the barium dimesitylborinate precursor did not contain β–barium borate. However, monophasic β–barium borate films were produced from heating the barium (crown ether) cyclotriboroxane precursor to temperatures between 600 and 700 °C for 1 hour. The six membered anionic borate ring is the key structural unit in β–barium borate. Since the

ring unit is already present in the barium (crown ether) cyclotriboroxane precursor lower temperature processing is needed, and substrate interaction becomes less likely. Ellipsometry was used to measure the index of refraction of the films. The index of refraction, measured by ellipsometry, was 1.51 for the film produced from barium dimesitylborinate. The index of refraction was 1.68 for the film produced from barium (crown ether) cyclotriboroxane.

1. INTRODUCTION

Nonlinear optics is the study of phenomena that occur as a result of the modification of the optical properties of a material system by the presence of light. The interaction of light with a non-linear optical material will cause the material's properties to change and the next photons that arrive will be affected by those altered properties.

The polarization of a molecule subject to an applied electric field is expanded in a power series in the applied field. The molecular polarization is given by:

$$p = \mu + \alpha*E + \beta*E*E + \gamma*E*E*E + \ldots$$

where μ is the permanent dipole moment of the molecule, α is the linear polarizability, and β and γ are the first and second hyperpolarizabilities. The polarization depends on the strength of the optical applied field, E. The higher order terms, β and γ, represent non-linear polarization and give rise to second and third order non-linear optical effects. Since $\alpha >> \beta,\gamma$, there were few observations of non-linear optical effects before the invention of the laser with its associated large electric fields [1]. The macroscopic polarization of a material is given by the following analogous equation:

$$P= Po + \chi^{(1)}*E + \chi^{(2)}*E*E + \chi^{(3)}*E*E*E + \ldots$$

P_o is the spontaneous polarization of the material. $\chi^{(1)}$ is the linear susceptibility. $\chi^{(2)}$ and $\chi^{(3)}$ are the second and third order susceptibilities, respectively. The term $\chi^{(2)}$ is responsible for second order non-linear optical effects and can only be exhibited by materials with a non-centrosymmetric structure. Since only asymmetric polarization leads to second order non-linear optical effects, these effects can only be induced by molecules lacking a center of symmetry. Incident light will induce the asymmetric

polarization of a second order non-linear optical material by the redistribution of electrons. The induced polarization generates an internal electric field that modifies the frequency of light as it passes through. If an intense light beam passes through a second order nonlinear optical material, light at twice the input frequency will be produced. This effect is termed second harmonic generation.

To understand why a second order non-linear optical material must have a non-centrosymmetric structure, the second order term, $P = \chi^{(2)}*E*E = \chi^{(2)}*E^2$, must be examined. If a material possesses inversion symmetry, then a sign change in E must be accompanied by a sign change in P [2]. By substituting negative values of P and E into the second order term the following equation is arrived at:

$$-P = \chi^{(2)}*-E*-E = \chi^{(2)}*E^2$$

By comparison to the original equation, it is determined that P must equal –P, which can only occur if the positive and negative values for P vanish identically. Therefore, $\chi^{(2)}$ must equal zero for symmetric materials.

β-barium borate (β-BBO) is one of the second order nonlinearly active materials. Two crystalline phases of BBO are known to exist, a high temperature α phase and a low temperature β phase. The transition temperature is equal to 925± 5 °C. The melting point occurs at 1095 °C. The α phase belongs to the space group R3c having a centric symmetry [3]. The β phase belongs to the space group R3 and is non-centrosymmetric [4]. β-barium borate consists of almost planar $(B_3O_6)^{3-}$ rings perpendicular to the polar c axis which are bonded together by barium atoms. The ionic group $(B_3O_6)^{3-}$ contains conjugated π orbitals which are believed to be the source of the second harmonic generation. The acentric symmetry of the barium cations in the β-barium borate structure

changes the electron density distribution of the boron-oxygen ring, thereby making principal contributions to the second harmonic generation [4]. The difference between the α and β form is the coordination of the barium by oxygen. In the case of α-BBO there are two distinct barium atoms. One has a ninefold oxygen coordination while the other is coordinated by six oxygen atoms [3]. In the case of β-BBO each barium atom has an eightfold oxygen coordination [5].

The β phase of BBO is characterized by relatively high second harmonic generation coefficients, a wide transparency range, a high optical damage threshold, and utility over a broad temperature range. It also has a broad phase matched region. Phase matching is a condition where the fundamental and second harmonic light waves reinforce each other. The refractive index experienced by the interacting waves as they propagate through the medium must match to achieve efficient second harmonic generation. Some physical properties of β-BBO are given in Table I [6].

Table I. Physical Properties of β-BBO

Crystal Structure	Trigonal (Rhombohedral) Symmetry: 3m(space group R3)
Cell Parameters	a = b = 12.532 A, c = 12.717 A
Transition Temperature (α→β phase)	925 ± 5°C
Melting Point	1095 °C
Transparency	189-3500 nm
Damage Threshold At 1.064 μm At 0.532 μm	 2 GW/cm^2 (7.5 ns pulse) 7 GW/cm^2 (250 ps pulse)
Phase Matchable SHG Range	189-1750 nm
SHG Coefficients	4-6 times higher than KDP depending on wavelength

β-BBO is well known in the bulk single crystal form. Single crystals of β-BBO are applied in laser systems to generate ultraviolet (UV) laser light using frequency doubling. Laser emission in the UV region is important for communications and high density data storage due to the shorter wavelength and smaller bit size that can be achieved [7]. Single crystals are also used in optical parametric oscillators as a means of obtaining tunable radiation [1].

Recently β-BBO has been considered for use as thin films in integrated non-linear optical devices. The various optical devices that thin films of β-BBO can be incorporated into include frequency converters, waveguides, switches, and storage devices. When generating second harmonics, the use of β-BBO non-linear optical waveguides is very attractive. The thin film is inherently a planar waveguide, eliminating other processing methods for formation of waveguides which can be detrimental to SHG coefficients [7].

In addition to the crystalline structure of the material being non-centrosymmetric, second order non-linear optical thin films must be transparent in the portion of the spectrum required for use, and the film must be able to withstand the high energy of the optical beam. The films must also be chemically homogenous and of high optical quality. Impurities or non-homogenous regions will cause undesired scattering centers in the film [7]. For example, inclusions in β-BBO can contribute to optical losses in films tested for waveguide applications.

Metallo-organic decomposition (MOD) is one method of obtaining thin films of β-BBO. Advantages of using MOD include a precise composition control and the ability to easily introduce dopants [8]. Metallo-organic chemical vapor deposition (MOCVD) is

another method that is used to produce thin films of β-BBO. MOCVD is advantageous due to its precise control of process conditions and high throughput. Another advantage is the ability to deposit films on complex geometries. The major problem with the MOCVD process is the difficulty of controlling the stoichiometry at the substrate surface. Dual precursors are commonly used to form β-BBO. Their different volatilities, densities, and thermal stabilities affect their decomposition rates. For example, an excess of boron must be used in the current deposition process of β-BBO [7]. If a single source precursor could be developed for MOCVD, it would be the desired method for obtaining β-BBO thin films. Until then, MOD is the preferred process.

Various researchers have been successful in preparing thin films of β-BBO by the metallo-organic decomposition and chemical vapor deposition methods. The past research has involved various chemical precursors and process conditions. Table II lists the related art and the researchers involved in this work. Thin films of β-BBO have also been successfully deposited by pulsed laser deposition and magneton sputtering [9-10].

In this research two novel precursors were developed for the formation of β-BBO thin films. A single source precursor, barium dimesitylborinate, $Ba[OB(Mes)_2]_2$, has been successfully synthesized and used with the MOD process. The original intent of the research was to develop a single source precursor for the MOCVD process. Since the new compound is not volatile the alternate MOD approach is used to fabricate films. The advantage of using a single source precursor is that the precise atomic ratio of the elements in the desired product can be incorporated in a single metallo-organic compound [16].

Table II. Prior Art for Beta- Barium Borate Thin Film Formation

Coating Process	Precursor(s)	Solvent	Process Conditions	Substrates	Authors
MOD/ Sol-Gel Dip Coating	Barium Ethoxide, 2,4,6-Triethoxycyclotriboroxane or Boron Triethoxide	Ethanol and 2-Ethoxyethanol	Calcined 1 hour at 350 °C in gas mixture of water and oxygen. Heat treated 1 hour at 550 °C in flowing oxygen.	Pt, Pt(111)/glass	Yogo, Kikuta, Niwa, Ichida, Nakamura, Hirano [11] [12]
MOCVD	Triisopropyl Borate, Ba(2,2,6,6-tetramethyl-3,5-heptanedionato)$_2$	Tetrahydrofuran and Tetragylme	Transported to reactor by liquid delivery system. Flash vaporized. Transported to substrate in nitrogen gas at 200 SCCM. Heated from 640 to 840 °C.	Fused silica, Pt, Sapphire, Silicon	Studebaker, Stauf, Baum, Marks, Zhou, Wong [7]
MOD/ Chemical Solution Deposition Spin Coating	Barium Acetate, Boric Acid	Acetic Acid, Ethanol, 2-methoxyethanol	Film dried in air at 250 °C for 30 min, calcined at 450 °C for 3 hr., Final heating at 500-800 °C for 1 hour in flowing oxygen.	Si(100) with SiO_2 layer	Kobayashi, Ogawa, Kuwabara [8] [13]
MOD/ Sol-Gel Spin Coating	$B(OC_4H_9)_3$ and/or $B_3O_3(OCH_3)_3$, $Ba(OCH_2CH_2OCH_3)_2$	Water and Toluene	Evaporation of water and solvents at 150 °C. Elimination of residual organics at 500 °C. Cystallization at 800 °C.	Silicon and Quartz	Nie, Lurin, Paz-Pujalt [6]
MOD/ Sol Gel Dip Coating or Drip Coating	Barium Ethoxide, Boron Triethoxide, Diethanolamine(DEA)	Ethanol	1 hour calcination at 350 °C. Final heat treatment from 400-900 °C. Both done in flowing oxygen.	Pt	Hirano, Yogo, Kikuta, Yamagiwa [14]
MOD/ Sol Gel Spin Coating	Barium Ligand (Prepared from Barium Hydroxide, 2-Ethylhexanoic Acid, and Toluene) and Boron Tributoxide	Methyl Alcohol and Glycerol	Precursor film heated to 800 °C for 5 minutes.	Fused silica	Nie, Paz-Pujalt [15]

The second novel precursor is a modification of one used in a method developed by Yogo et al [11]. A precursor solution is prepared from $(OB^*OEt)_3$, barium metal, ethanol, and 18-crown-6 (crown ether). The advantage of this method is that the basic structural unit for β-BBO, the six-membered borate ring, is incorporated in the precursor. In the precursor solution reported by Yogo, 2-ethoxyethanol is used as a stabilizer. In contrast to the reported method, a crown ether, 18-crown-6, is used here in place of 2-ethoxyethanol. The crown ether surrounds barium atoms and saturates their coordination sphere. The main advantage of using crown ether in the precursor solution is lower temperature β-barium borate formation. The use of 2-ethoxyethanol creates polymeric bridges between barium atoms which requires a higher temperature to overcome them and obtain the beta form. The novel precursor containing the crown ether is believed to be monomeric in nature and should thus require less temperature for transformation. Other advantages of using a crown ether include the ease of characterizing the precursor and its greater stability.

2. EXPERIMENTAL

2.1 Materials

Dimesitylborinic Acid 98%, triethylborate 99%, boron oxide 99.999%, barium metal (dendritic pieces) 99.9%, 18-crown-6 99%, and barium pieces 98% were obtained from Aldrich and used as received. 2-Ethoxyethanol and ethanol were obtained from Aldrich and Pharmca Products, respectively. Both were dried over barium metal and distilled. Barium hydride 99.5% was obtained from Alfa Aesar and was also used as received. Tetrahydrofuran was obtained from J.T. Baker and dried over calcium hydride.

2.2 Synthesis of Barium Dimesitylborinate, $Ba[OB(Mes)_2]_2$, Single Source Precursor

The single source precursor, $Ba[OB(Mes)_2]_2$, was prepared from barium hydride and dimesitylborinic acid.

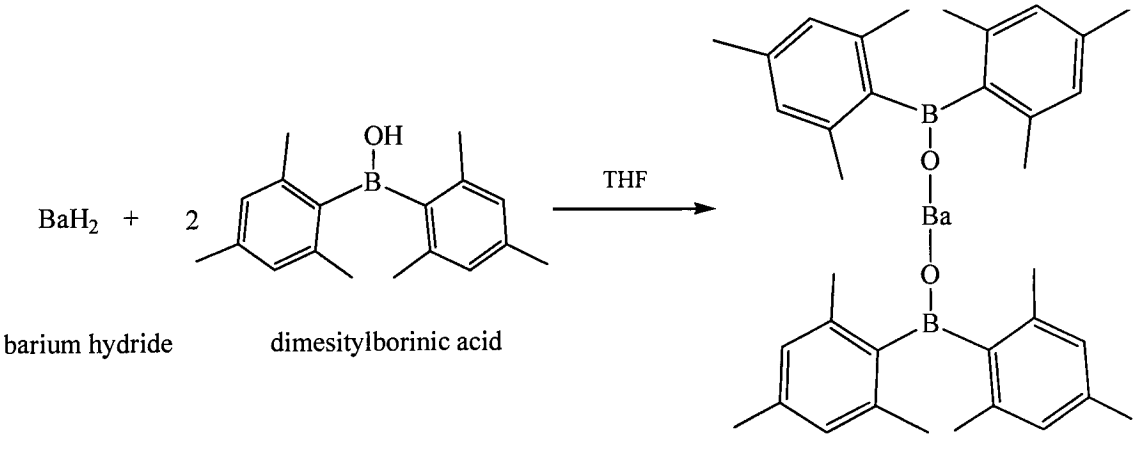


Figure 1. Synthesis of $Ba[OB(Mes)_2]_2$ Single Source Precursor

Tetrahydrofuran (THF) was used as the solvent for this reaction. The THF was dried over calcium hydride and distilled into a round bottom flask containing a stopcock. Following distillation the stopcock was closed to allow transport of the round bottom flask without exposure to moisture. The distillation setup also included a drying tube filled with dessicant to ensure the dried solvent remained free of moisture.

The round bottom flask containing the dried THF was brought to a glove bag to add the solid reactants, BaH_2 and Mes_2BOH, under nitrogen. BaH_2 must be handled under nitrogen to avoid $Ba(OH)_2$ formation. Mes_2BOH must also by handled under nitrogen due to its hydroscopic nature. Since BaH_2 readily forms $Ba(OH)_2$, some of the starting material will in fact be $Ba(OH)_2$. In addition, some of the BaH_2 will form $Ba(OH)_2$ from exposure to moisture picked up by the Mes_2BOH. To correct for these problems it was determined that a 100% excess of BaH_2 must be used to arrive at the desired product. Instead of a 1:2 molar ratio of BaH_2 to Mes_2BOH a 1:1 molar ratio was found necessary to give a good yield of $Ba[OB(Mes)_2]_2$. Thus, 0.26 grams (1.9 mmoles) of BaH_2 and 0.50 grams (1.9 mmoles) of Mes_2BOH were added to approximately 25 mL of dried THF and heated at reflux for 48 hours under nitrogen.

At this point in the reaction the solution appears to be somewhat cloudy. The cloudiness can be attributed to $Ba(OH)_2$ that formed from the BaH_2 either prior to the reaction or as a result of contact with the adsorbed water on Mes_2BOH. The solution is taken again to the glove bag where it is filtered through a sintered glass frit under nitrogen. The filtering step removes any $Ba(OH)_2$ and/or unreacted BaH_2. Following the filtering step, a rubber stopper is put on top of the filter flask and the THF is removed

under reduced pressure. After the solvent was removed the product, $Ba[OB(Mes)_2]_2$, remains. The $Ba[OB(Mes)_2]_2$ is collected from the filter flask using a microspatula and immediately placed in a plastic storage vial. The storage vial is then put into the glove box until it is to be used. The percent yield of the product varies between 75 and 85%. The color of the resulting solid is a yellowish white. The melting point range of the solid is approximately 158-160 °C.

2.2.1 Thin Layer Chromatography of Solution

Reverse phase thin layer chromatography (TLC) is performed on the solution to determine when the reaction is complete. A Baker Si250F TLC Plate is used. A good eluent for this experiment consists of a mixture of 90% hexanes and 10% toluene. One side of the TLC plate is spotted with the reaction solution and the other with dimesitylborinic acid dissolved in THF. After 48 hours of reflux the test confirms that the borinic acid is no longer present in the reaction solution.

2.2.2 Characterization of $Ba[OB(Mes)_2]_2$ (s)

The product is initially tested for the presence of barium by the following procedure. $Ba[OB(Mes)_2]_2$ (s) is dissolved in toluene in a test tube. HCl (aq) is then added and the mixture is shaken vigorously to form $BaCl_2$ (aq). The aqueous phase of the mixture containing $BaCl_2$ (aq) and HCl (aq) is pipetted out. This portion is reacted with Na_2SO_4 (aq) to form a solid precipitate of $BaSO_4$ (s). The presence of the $BaSO_4$ precipitate confirms the presence of barium.

After the above test confirms the presence of barium, the product was subjected to a variety of analytical techniques. The sample is tested by proton nuclear magnetic resonance (NMR), infrared (IR) spectroscopy, elemental analysis, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC).

2.3 Preparation of Precursor from 2,4,6-Triethoxycyclotriboroxane and Barium (Crown Ether) Ethoxide

A precursor solution was prepared from 2,4,6-triethoxycyclotriboroxane and barium (crown ether) ethoxide. The steps involved in the preparation are shown in Figure 2.

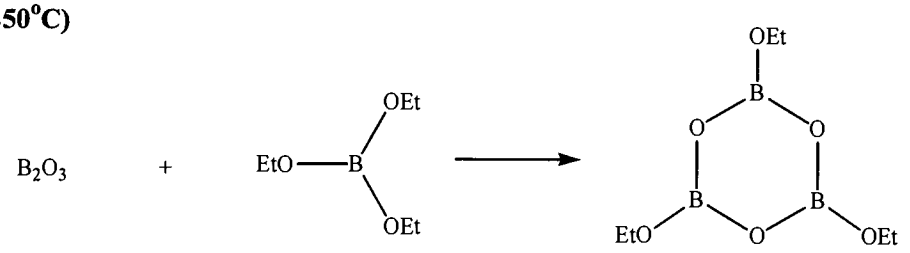
2.3.1 Preparation of 2,4,6-Triethoxycyclotriboroxane

A 2,4,6-triethoxycyclotriboroxane solution was prepared from triethylborate and boron oxide according to the literature [17].

$$(EtO)_3B\ (aq) + B_2O_3\ (s) \rightarrow (OB^*OEt)_3\ (\text{Sealed Tube 250 °C})$$

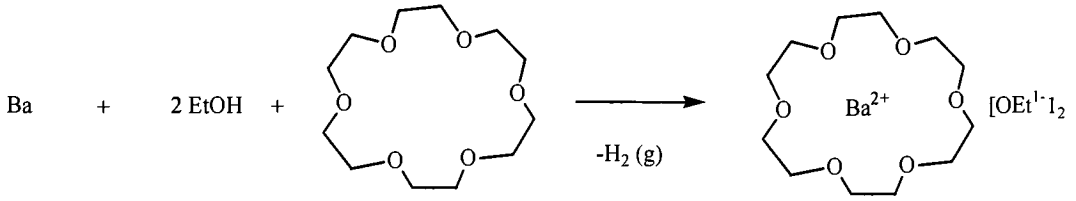
B_2O_3, 1.49 grams (21.0 mmoles), and $(EtO)_3B$, 3.56 mL (21.0 mmoles), are sealed in a dried reaction tube under dynamic vacuum. The reaction tube is dried by pulling a vacuum on the tube and heating along its length with a gentle flame. Connected to the reaction tube is a short length of hose connected to a three way valve. On the opposite side of the three way valve is a longer length of hose connected to the vacuum pump.

STEP #1 Preparation of 2,4,6-Triethoxycyclotriboroxane (Performed in Sealed Tube at 250°C)



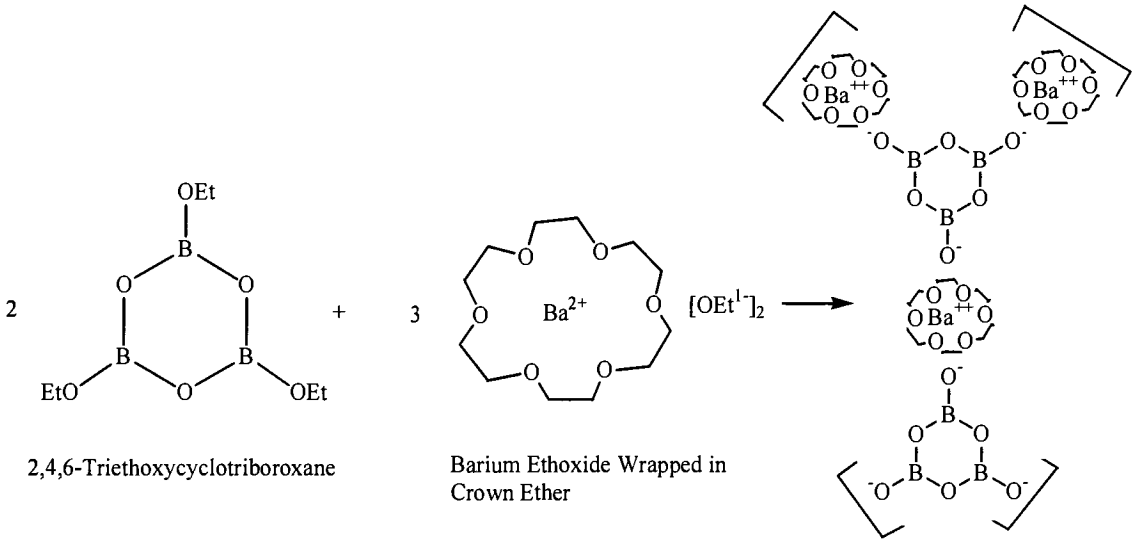
Boron Oxide Triethylborate 2,4,6-Triethoxycyclotriboroxane

STEP #2 Preparation of Barium Ethoxide Wrapped in Crown Ether



Ba Metal Ethanol 18-Crown-6 Barium Ethoxide Wrapped in Crown Ether

STEP #3 Preparation of Precursor Solution (Refluxed for 20 hours in Ethanol)



2,4,6-Triethoxycyclotriboroxane Barium Ethoxide Wrapped in Crown Ether Precursor

Figure 2. Formation of Barium (Crown Ether) Cyclotriboroxane Precursor

After heating, the valve is closed to maintain vacuum and prevent moisture from entering the tube. The vacuum hose is removed from the three way valve on the vacuum pump side and the remaining apparatus is brought to the glove box where the reaction components are added. At this point only nitrogen is allowed to enter the tube. The closed valve is replaced on the tube and the assembly is brought to a vacuum pump where a vacuum is reapplied. The valve is opened again to dynamic vacuum and the tube containing the reactants is sealed with a torch. The reaction tube is then placed in a tube furnace and heated to 250 °C for a period of 20 hours. The resulting product is a clear, colorless liquid of 2,4,6-triethoxycyclotriboroxane. The boroxane was purified by dissolving in dried THF and filtering through a sintered glass frit. The solvent was then removed under reduced pressure. A purified clear liquid product, 4.50 grams (20.9 mmoles), was obtained. The yield of the experiment was ~98%. The resulting liquid was tested by FT-IR spectroscopy.

2.3.2 Preparation of Barium (Crown Ether) Ethoxide Solution

Approximately 125 mL of ethanol was dried over barium metal and distilled. The dried ethanol was then taken to the glove bag to add the reactants under nitrogen. To the dried ethanol 4.29 grams (31.2 mmoles) of barium metal were added. The barium metal instantly reacted with the ethanol to form barium ethoxide. Heat was produced and hydrogen gas was released as a result. Crown ether, 8.25 grams (31.2 mmoles), is also added. The solution is heated at reflux under nitrogen for one hour to produce the barium (crown ether) ethoxide solution. The molecular weight of the resulting compound,

[Ba(18-crown-6)$(OEt)_2$], in solution is 491.74 g/mol. The solution is initially clear, but does change to a yellowish color after 15 minutes.

2.3.3 Isolation and Characterization of Barium (Crown Ether) Ethoxide Powders

Another ethanol solution was produced with the same molar ratio of barium to crown ether. This time the solvent was evaporated under reduced pressure and the solid barium (crown ether) ethoxide was collected for analysis. The resulting powder was stored in the glove box under nitrogen. The yield, approximately 15 grams, was nearly 100%. Samples of the powders were analyzed by proton NMR, IR spectroscopy, DSC, TGA, and mass spectroscopy.

2.3.4 Preparation of Precursor Solution from 2,4,6-Triethoxycyclotriboroxane and Barium (Crown Ether) Ethoxide Solution

A portion of 2,4,6-triethoxycyclotriboroxane, 4.5 grams (20.9 mmoles), was dissolved in 50 mL of ethanol dried over barium metal. This solution was then added to the barium (crown ether) ethoxide solution containing 4.29 grams (31.0 mmoles) of barium. The mixture containing a 3:2 molar ratio of barium to 2,4,6 triethoxycyclotriboroxane was then heated at reflux for 20 hours. A homogeneous precursor solution of barium (crown ether) cyclotriboroxane is produced as a result. The solution was a yellowish color.

2.3.5 Isolation and Characterization of Barium (Crown Ether) Cyclotriboroxane Powders

Half of the barium (crown ether) cyclotriboroxane precursor solution was hydrolyzed with excess water while the other half was not. The solvent and/or water was then removed from each sample by applying a vacuum to a flask containing the solution while the contents are heated in a hot oil bath kept less than 100 °C. An acetone dry ice bath is used to condense the solvent vapor in a solvent trap. The resulting powders are collected from the flask with a microspatula and stored in a glass vial. The appearance of the hydrolyzed and non-hydrolyzed powders differed. The hydrolyzed powder forms aggregates and is cream colored throughout. The non-hydrolyzed powder is flaky and consists of orange and cream colors. The samples were analyzed by IR spectroscopy, TGA, DSC, and elemental analysis.

2.4 Preparation of Precursor Powders Using 2-Ethoxyethanol as Reported by Yogo et. al.

A precursor solution was prepared according to the published work to verify their results [11]. The precursor solution was prepared in the exact same manner as the precursor described in section 2.3 except for the preparation of the barium alkoxide solution. In the method described by Yogo the barium alkoxide was prepared from ethanol and 2-ethoxyethanol. A 5:1 molar ratio of ethanol to 2-ethoxyethanol was used.

Barium metal was added to the solution of ethanol and 2-ethoxyethanol and heated at reflux to produce a barium alkoxide solution. In this method no crown ether is used. Just as before the 2,4,6 triethoxycyclotriboroxane is dissolved in dried ethanol and added to the alkoxide solution. After 20 hours of reflux the solution is ready for use. The solution is hydrolyzed and solvents and water are removed yielding powders. The powders were analyzed with TGA and DSC.

2.5 Heat Treatment of Precursor Powders to form β- Barium Borate

The precursor powders produced by the various methods were heated to obtain the crystalline form of beta-barium borate. The heat treatment apparatus consisted of an electric furnace equipped with a gas input nozzle on the backside. Oxygen was used as a flow gas during the experiments. The flow was measured to be approximately 250 cm^3/sec. For the barium dimesitylborinate single source precursor oxygen was required to produce the β-BBO. In the case of the barium (crown ether) cyclotriboroxane precursor the gas aided in calcination. The precursors were placed in a porcelain crucible inside the glove box and transferred to an oven preheated to 150°C. The heating cycle for the two precursors varied, as follows.

2.5.1 Heat Treatment of the Barium Dimesitylborinate Single Source Precursor Powder to form β- Barium Borate

$Ba[OB(Mes)_2]_2$ was heated under oxygen flow to form β-barium borate. Figure 3 shows the chemistry involved its formation. Oxygen flow is required in the reaction and is supplied as a gas.

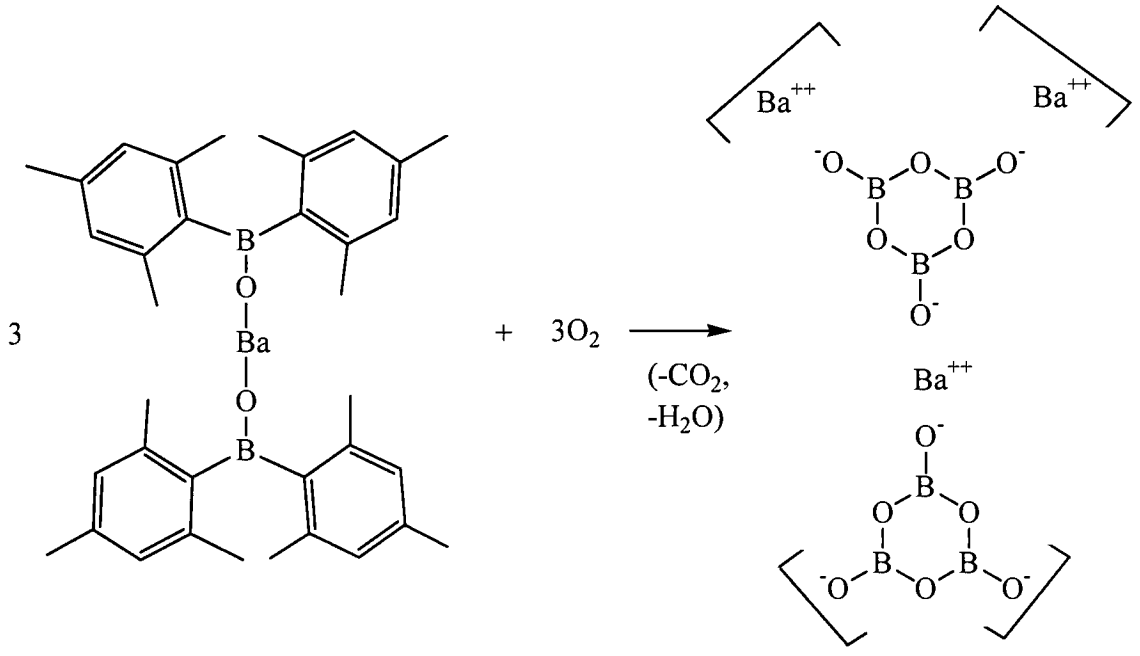


Figure 3. Formation of β-Barium Borate

A slow heating cycle was found to be necessary to form the β-BBO. It is presumed that the organics leave the compound at a slow rate. The heating cycle takes 4 hours and is as follows:

Temperature	Duration
150 °C	30 min.
175 °C	30 min.
250 °C	30 min.
350 °C	30 min.
550 °C	30 min.
650 °C	30 min.
800 °C	1 hour

Upon reaching 175°C the solid has melted. Above 250 °C the material begins to darken in color. At 550 °C the material is a grayish colored solid. At higher temperatures the solid rearranges to form the β-BBO. The resulting powder was characterized using x-ray diffraction to verify that the desired crystalline phase of barium borate was produced.

2.5.2 Heat Treatment of Barium (Crown Ether) Cyclotriboroxane Powder and Powder Produced using 2-Ethoxyethanol as Reported by Yogo

The barium (crown ether) cyclotriboroxane precursors and the precursor prepared according to Yogo (containing 2-ethoxyethanol) were both heated in the same manner. The samples in crucibles were placed in the preheated oven under oxygen flow. The temperature was raised to 250 °C and held for 30 minutes. The powders were then calcined at 350 °C for one hour. Following calcination the powders were brought to the final temperature and heated for one hour. The final heating temperatures used were 550 °C, 650 °C, and 750 °C. The powders heated at these temperatures were studied by x-ray diffraction to determine the temperature of the transition to the β-BBO phase.

2.6 Preparation of Precursor Thin Films on Si (100) Substrates

Solutions containing barium dimesitylborinate and barium (crown ether) cyclotriboroxane precursors were prepared and applied to clean silicon substrates. The solutions were applied using a spin coating technique.

2.6.1 RCA Cleaning of Silicon Wafers for Spin Coating

The RCA process was used to clean silicon (100) wafers and remove the any oxide present. The wafers were initially placed in a tank containing 4500 mL of deionized (DI) water, 300 mL of NH_4OH, and 900 mL of H_2O_2 for 10 minutes. This tank was held at 80°C. The wafers are then removed and rinsed with DI water for 5 minutes. Following the rinse the wafers are dipped in a 50:1, water to HF, solution for 1 minute. Again the wafers are rinsed for 5 minutes. They are now placed into a tank containing 4500 mL of DI water, 300 mL of HCl, and 900 mL of H_2O_2 for 10 minutes. This tank is held at 75 °C. The wafers are finally rinsed for 5 minutes and dried. This process removes the glass layer of SiO_2 on the substrate surface and also serves as a cleaning step.

2.6.2 Preparation of Barium Dimesitylborinate (Single Source Precursor) Spin Coating Solution and Application to Substrate

Solid $Ba[OB(Mes)_2]_2$, 1.33 grams (1.99 mmoles), was dissolved in 20 mL of dry THF to prepare the precursor solution. The THF was dried over calcium hydride and distilled prior to use. The resulting 20 mL of solution (0.099 M $Ba[OB(Mes)_2]_2$) was used to coat 10 substrates, each coating requiring 2 mL. The solution should be stored in a glass vial under nitrogen for use at a later time.

The spin coater is programmed to accelerate at 100 RPM/sec to 750 RPM. The duration at 750 RPM is 1 minute. The speed is then decelerated to zero at a rate of 100 RPM/sec. Once the program is setup properly a wafer should be placed on the chuck

located on the moveable arm of the instrument. The arm should be moved horizontally so the wafer is directly above the rotational platform. The lifter should be raised to pick up the wafer and gently lower it to the platform. The platform provides a vacuum which holds the wafer in place. The precursor solution, 2 mL, should then be applied evenly over the substrate surface from a pipette. After the solution has been applied the spin coater program is initiated.

2.6.3 Preparation of Barium (Crown Ether) Cyclotriboroxane Spin Coating Solution and Application to Substrate

The barium (crown ether) cyclotriboroxane spin coating solution was prepared in a similar manner to that of barium dimesitylborinate. Barium (crown ether) ethoxide, 11.0 grams (0.0223 moles), was dissolved in 75.0 mL of dried ethanol. To this solution, $(OB^*OEt)_3$, 3.22 grams (0.0149 moles), was added. The resulting solution was heated at reflux yielding an expected 10.9 grams (0.00746 moles) of precursor. The concentration of the final spin coating solution is 0.0995 M. As with the barium dimesitylborinate solution the silicon wafer required approximately 2 mL to be uniformly coated. Ten substrates were coated in the same manner as above. The spin coater program explained in section 2.6.2 was found to work for this solution as well.

2.6.4 Heat treatment of Precursor Films on Si (100) Wafers

The films of both precursors were heated in the same manner. After the solutions have been spin coated on the wafers, the films are calcined at 300 °C for 1 hour under flowing oxygen. The oxygen flow was measured to be 250 cm^3/s. The calcination step removes organics from the film.

The next step in the process was to heat the films at the desired temperature and duration of time. Four of the wafers from both methods were heated at 850°C for 1, 5, 10, and 30 minutes. This test is an attempt to determine how quickly β–BBO forms at elevated temperatures. A second test requires five wafers from both methods. These wafers are heated for 1 hour at 500, 550, 600, 650, and 700°C. This test is performed to determine the onset and completion of β–BBO formation.

Characterization was performed on these samples by thin film x-ray diffraction and ellipsometry. Optical microscopy was also used to monitor crystallization.

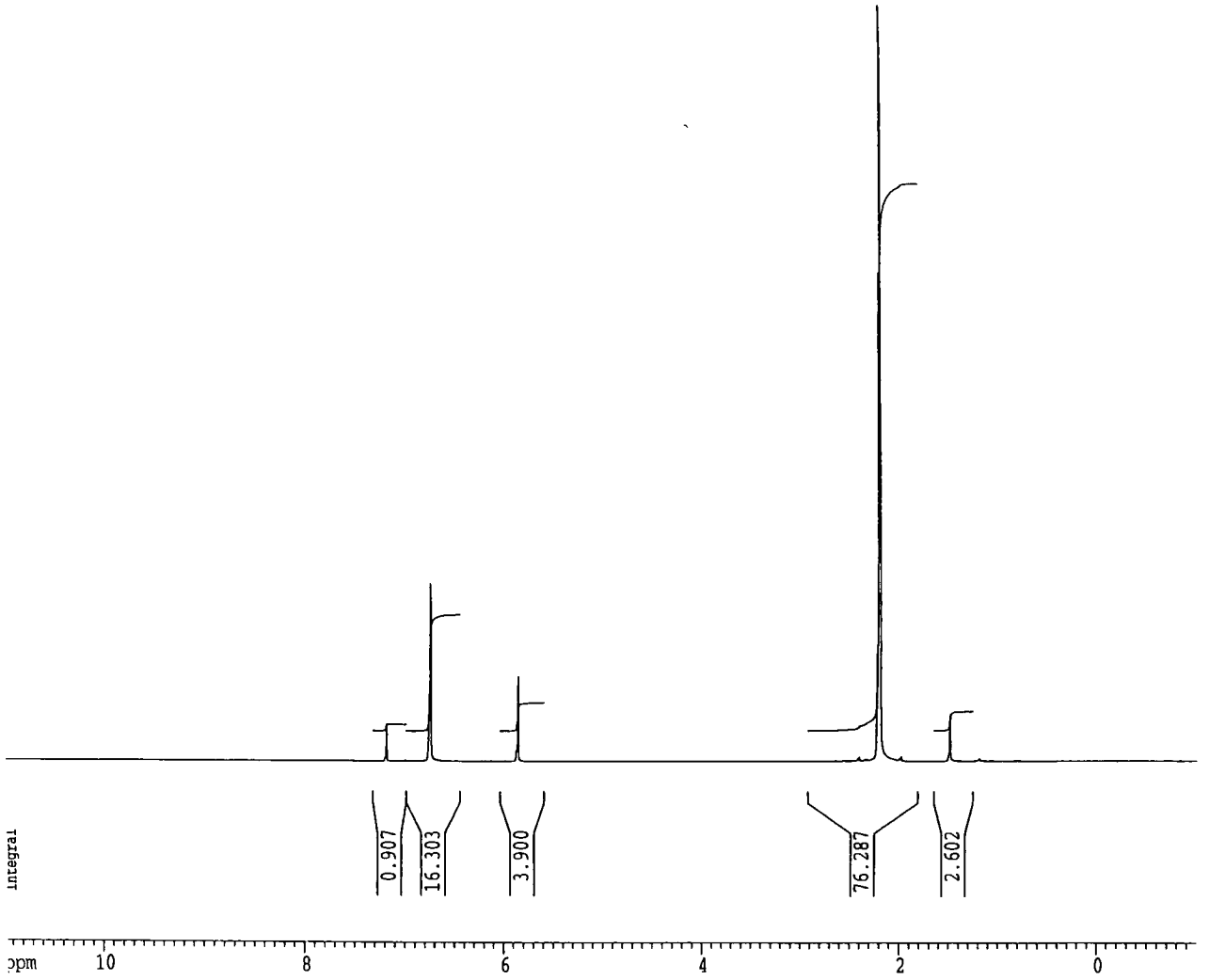
3. RESULTS AND DISCUSSION

3.1 Characterization of $Ba[OB(Mes)_2]_2$ Single Source Precursor

$Ba[OB(Mes)_2]_2$ was successfully prepared by the procedure described. Various characterization techniques are used for confirmation.

3.1.1 Proton NMR of Dimesitylborinic Acid Sample

Proton nuclear magnetic resonance was performed on dimesitylborinic acid as shown in Figure 4. Peaks at 7.18 and 1.47 ppm are attributed to the deuterated chloroform used as the NMR solvent as shown in Figure 5. The peak at 6.75 ppm arises from the four aromatic protons (directly connected to the rings) of the mesityl groups. The peak at 5.85 ppm arises from the hydroxy proton (the single proton attached to the lone oxygen in the compound). The peak at 2.20 ppm corresponds to the eighteen protons representative of the methyl groups. Figure 6 shows the chemical shifts for dimesitylborinic acid protons. The integrated areas of the peaks in Figure 4 are at the appropriate ratios for the expected number of protons in the sample. The ratio of the aromatic proton peak area to the methyl proton peak area is 4:19. This ratio is very close to that which is expected (4:18).

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DE                 6.00 usec
TE                300.0 K
D1             1.00000000 sec

============ CHANNEL f1 ============
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PL1                 -3.00 dB
SFO1          300.1318534 MHz

F2 - Processing parameters
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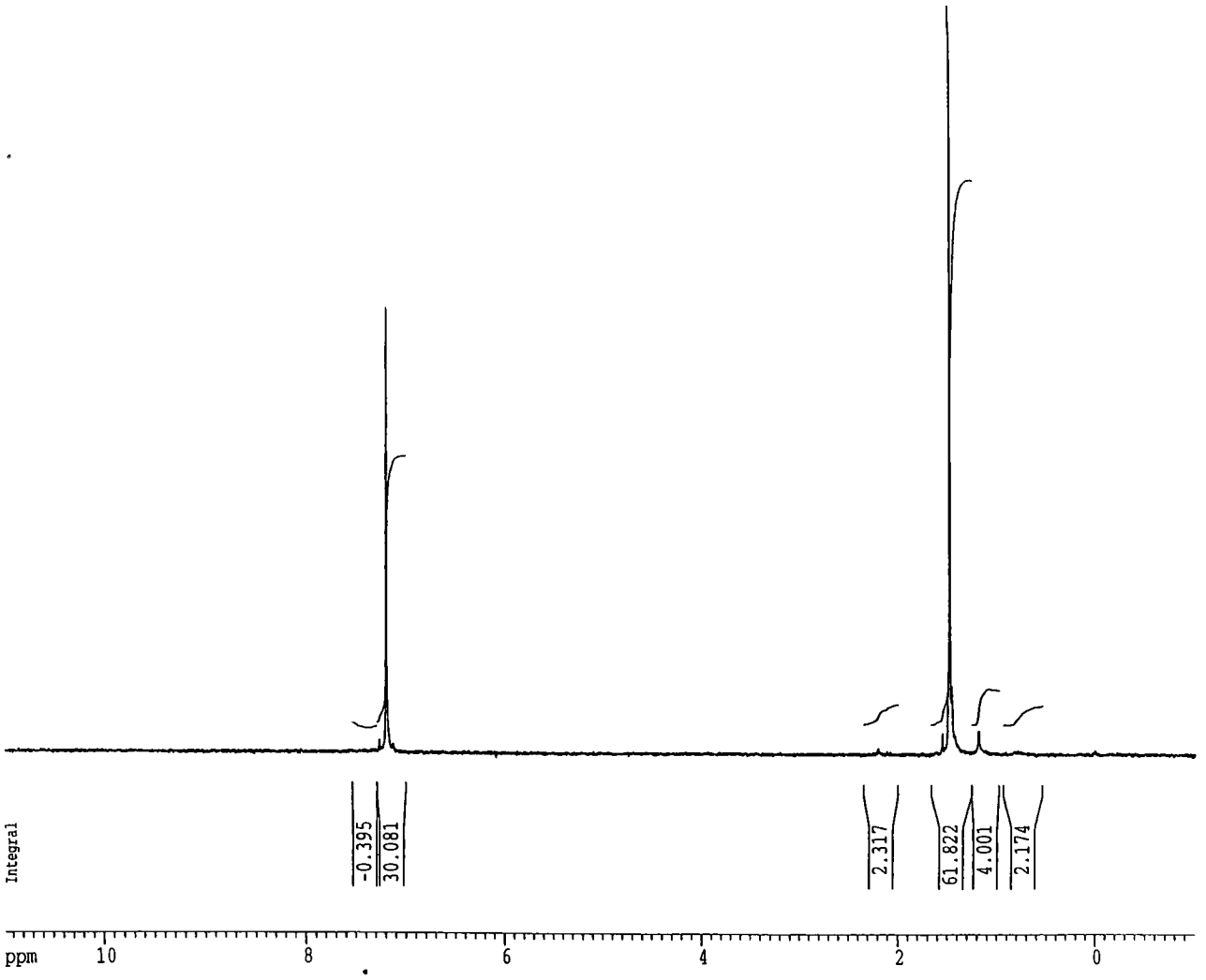
SF            300.1300306 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P               11.000 ppm
F1               3301.43 Hz
F2P               -1.000 ppm
F2              -300.13 Hz
PPMCM            0.60000 ppm/cm
HZCM           180.07802 Hz/cm
```

Figure 4. Proton NMR Spectrum for Dimesitylborinic Acid in Deuterated Chloroform

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FIDRES          0.094190 Hz
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DE                 6.00 usec
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PL1                -3.00 dB
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F2 - Processing parameters
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PC                  1.00

1D NMR plot parameters
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F1               3301.43 Hz
F2P                -1.000 ppm
F2               -300.13 Hz
PPMCM            0.60000 ppm/cm
HZCM           180.07802 Hz/cm
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Figure 5. Proton NMR Spectrum for Deuterated Chloroform

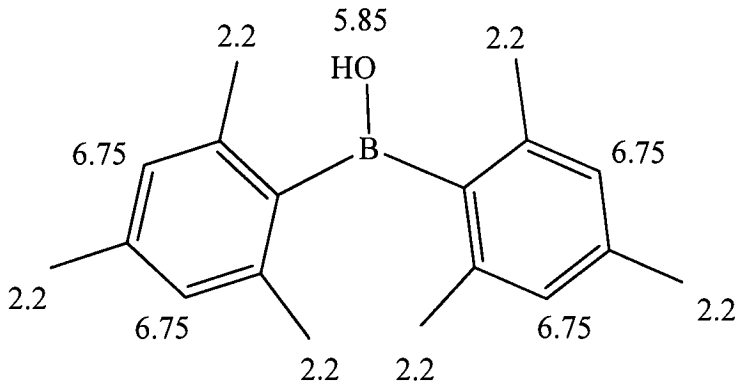
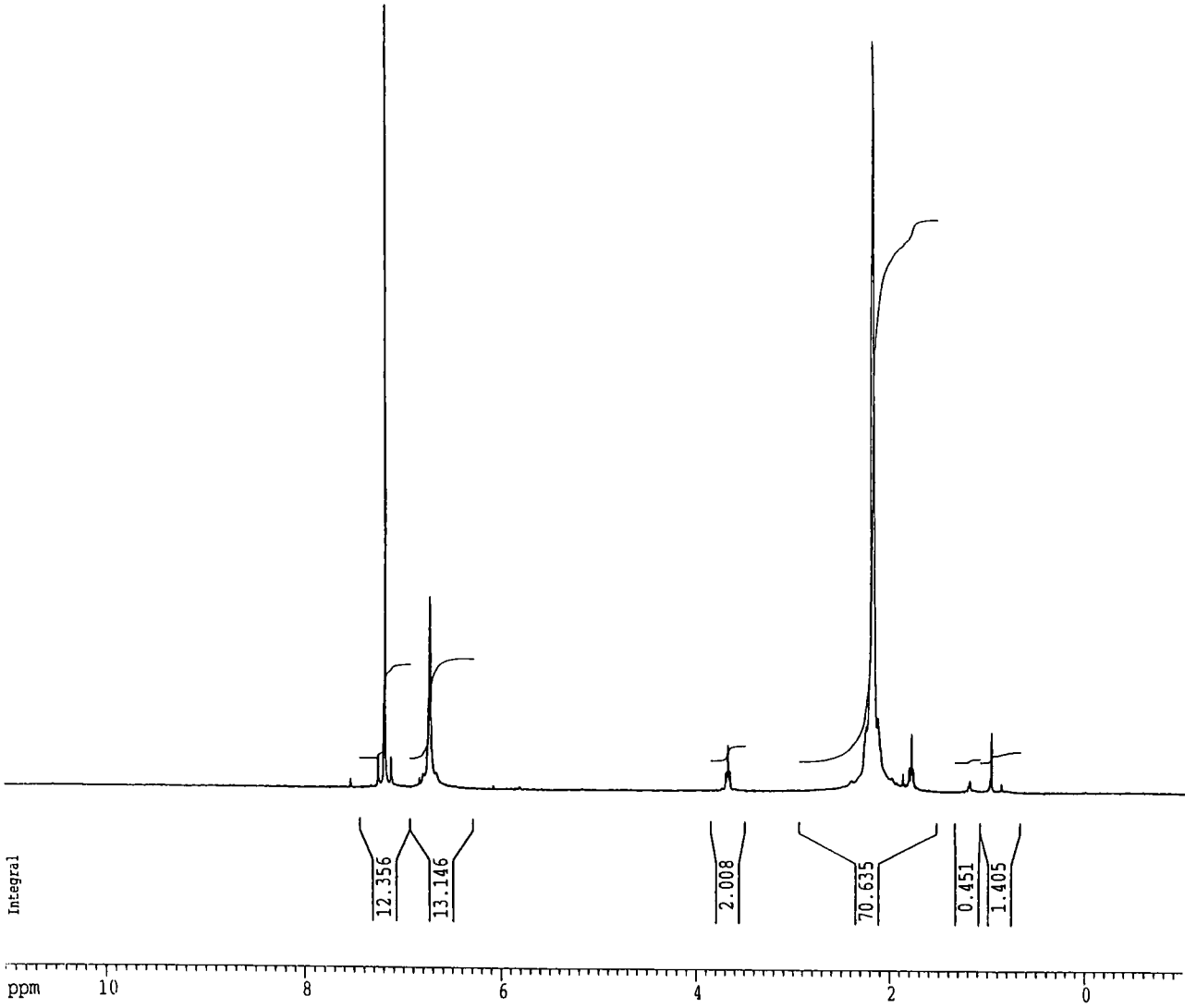


Figure 6. Chemical Shifts for Dimesitylborinic Acid Protons

3.1.2 Proton NMR of $Ba[OB(Mes)_2]_2$

The proton NMR spectrum of the $Ba[OB(Mes)_2]_2$ was also recorded in deuterated chloroform. Figure 7 is an example of a typical NMR spectrum for this precursor compound. The major difference between the NMR spectrum of dimesitylborinic acid and $Ba[OB(Mes)_2]_2$ is the lack of the proton from the –OH group located at 5.85 ppm. Also, peaks are present at 1.77 and 3.68 ppm from residual tetrahydrofuran used in the chemical reaction (See Figure 8). Peaks at 7.18 and 1.20 ppm arise from the deuterated chloroform (See Figure 5). The remaining peaks located at 2.20 and 6.75 ppm are identical to those found in the dimesitylborinic acid sample. The integration ratio (13:70) is close to the expected ratio of 8:36. Since the hydroxy proton of Mes_2BOH at 5.85 ppm is no longer present it can be assumed that $Ba[OB(Mes)_2]_2$ has been successfully synthesized.

3.1.3 Proton NMR of Dried $Ba[OB(Mes)_2]_2$

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FIDRES          0.094190 Hz
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RG                 724.1
DW                81.000 usec
DE                 6.00 usec
TE                300.0 K
D1             1.00000000 sec

============ CHANNEL f1 ============
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PL1                -3.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
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SF           300.1300273 MHz
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GB                     0
PC                  1.00

1D NMR plot parameters
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F1P               11.000 ppm
F1               3301.43 Hz
F2P               -1.000 ppm
F2               -300.13 Hz
PPMCM            0.60000 ppm/cm
HZCM           180.07802 Hz/cm
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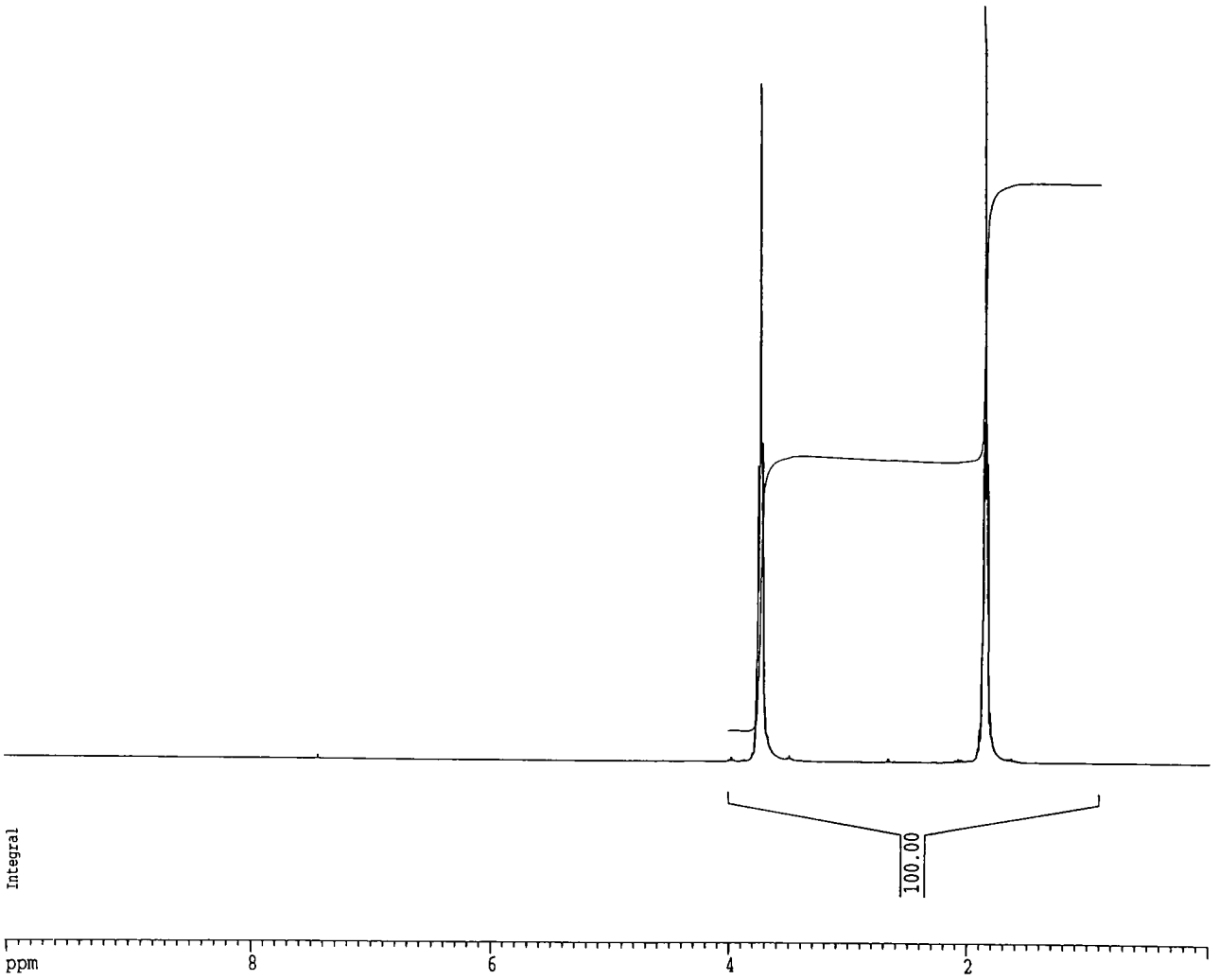
Figure 7. Proton NMR Spectrum for $Ba[OB(Mes)_2]_2$ in Deuterated Chloroform

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SOLVENT            CDCl3
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DS                     2
SWH             6172.839 Hz
FIDRES          0.094190 Hz
AQ              5.3084660 sec
RG                  22.6
DW                81.000 usec
DE                 6.00 usec
TE                300.0 K
D1             1.00000000 sec

============ CHANNEL f1 ============
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P1                   9.50 usec
PL1                 -3.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
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SF           300.1299526 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00

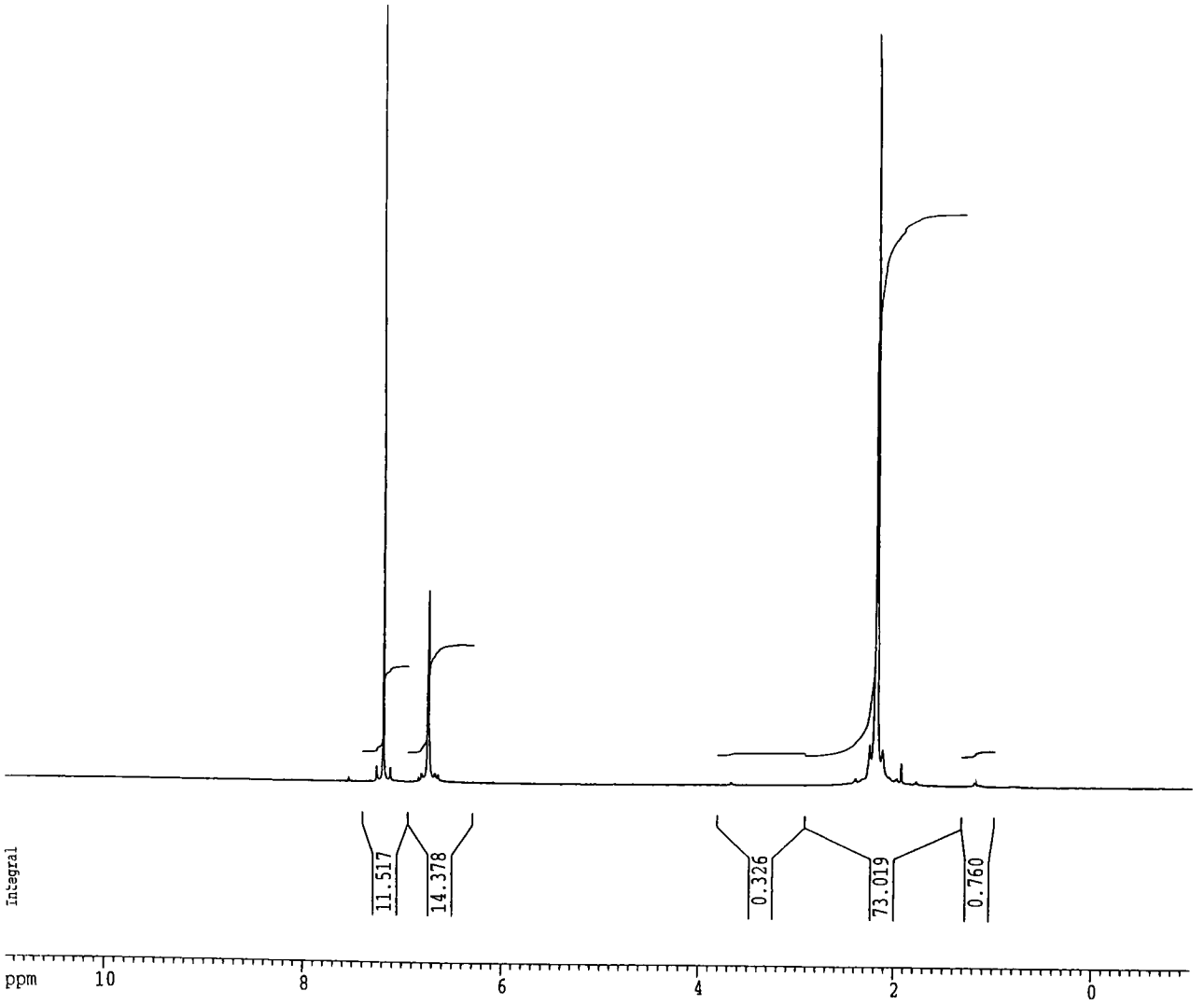
1D NMR plot parameters
CX                  20.00 cm
F1P                10.017 ppm
F1                 3006.43 Hz
F2P                -0.007 ppm
F2                 -2.13 Hz
PPMCM           0.50121 ppm/cm
HZCM          150.42793 Hz/cm
```

Figure 8. Proton NMR Spectrum for THF in Deuterated Chloroform

When a sample of the $Ba[OB(Mes)_2]_2$ was dried for 72 hours in an Abderhalden apparatus the amount of solvent (THF) was greatly decreased. Water was heated at reflux in the Abderhalden to maintain a 100 ^{o}C temperature. The combination of increased temperature and vacuum removes residual solvents from the precursor. Similar results are obtained by simply leaving a portion of the compound exposed to air for the same amount of time. There has been great difficulty in achieving 100% removal of the solvent. Drying the sample is a necessary step for elemental analysis of samples. The NMR spectra for the dried samples can be seen in Figures 9 and 10.

3.1.4 IR Spectroscopy on $Ba[OB(Mes)_2]_2$

The infrared spectrum of neat $Ba[OB(Mes)_2]_2$ is shown in Figure 11. The bands located at 2978.20, 2914.47, and 2852.71 cm^{-1} are due to the C-H stretching vibrations in methyl groups attached to the benzene rings. The bands at 2978.20 and 2914.47 cm^{-1} are caused by asymmetric and symmetric stretching, respectively. The band at 2852.71 cm^{-1} is caused by deformation vibrations. The band at 1605.74 cm^{-1} is caused by the stretching vibration of the C=C bonds in the benzene rings. The bands at 1422.40, 1257.93 cm^{-1} are from the vibrations of the boron-benzene bonds. The band at 1365 cm^{-1} is caused by stretching vibration between the boron and oxygen bonds. The C-H bonds on the benzene rings give rise to bands at 1197.08 and 829 cm^{-1} due to in plane and out of plane bending [18]. Bands for the Ba-O vibrations do not appear on this spectrum. The low vibration frequency caused by the large barium atom is off the scale of this spectrum.

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FIDRES           0.094190 Hz
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DE                  6.00 usec
TE                 300.0 K
D1              1.00000000 sec

============ CHANNEL f1 ============
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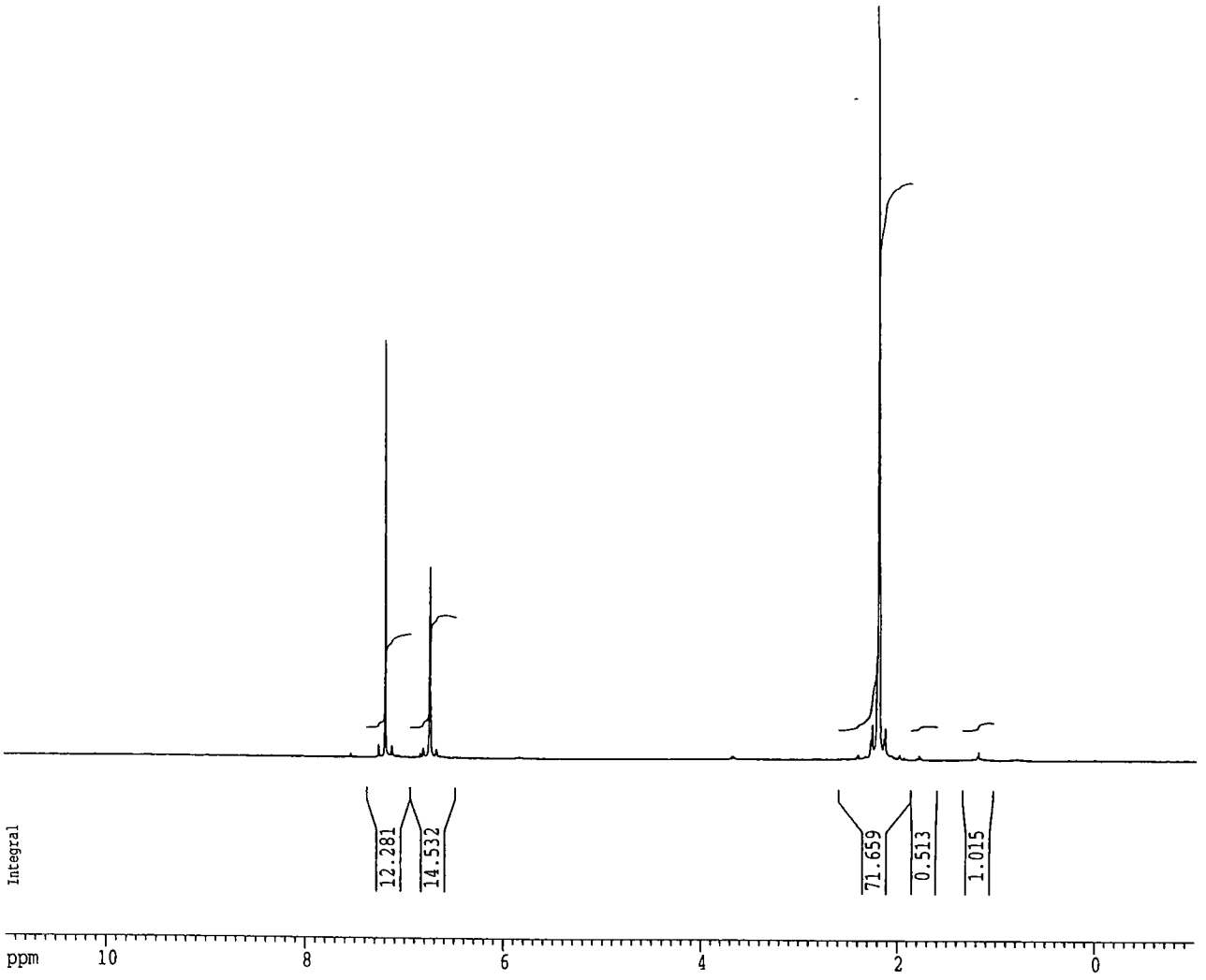
P1                   9.50 usec
PL1                 -3.00 dB
SFO1          300.1318534 MHz

F2 - Processing parameters
SI                  32768
SF            300.1300280 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  20.00 cm
F1P                11.000 ppm
F1                3301.43 Hz
F2P                -1.000 ppm
F2                -300.13 Hz
PPMCM             0.60000 ppm/cm
HZCM            180.07802 Hz/cm
```

Figure 9. Proton NMR Spectrum of $Ba[OB(Mes)_2]_2$ Dried in Abderhalden

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TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              6172.839 Hz
FIDRES           0.094190 Hz
AQ               5.3084660 sec
RG                 724.1
DW                81.000 usec
DE                 6.00 usec
TE                300.0 K
D1            1.00000000 sec

============ CHANNEL f1 ============
NUC1                   1H
P1                  9.50 usec
PL1                -3.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                  32768
SF           300.1300270 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  20.00 cm
F1P                11.000 ppm
F1                3301.43 Hz
F2P               -1.000 ppm
F2                -300.13 Hz
PPMCM             0.60000 ppm/cm
HZCM            180.07802 Hz/cm
```

Figure 10. Proton NMR Spectrum of $Ba[OB(Mes)_2]_2$ after Air Exposure

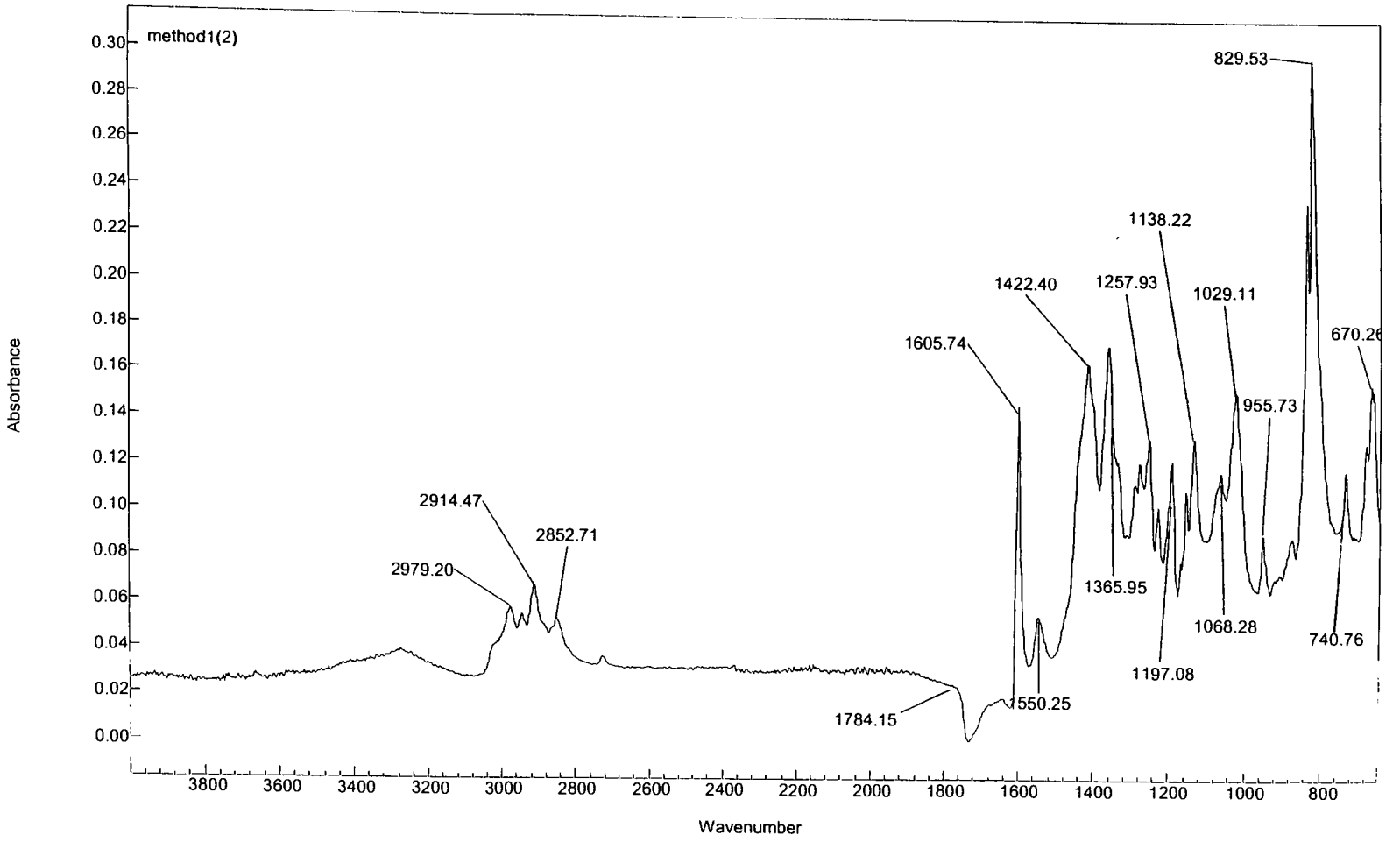


Figure 11. IR Spectrum for $Ba[OB(Mes)_2]_2$

3.1.5 Elemental Analysis of $Ba[OB(Mes)_2]_2$

Elemental analysis was performed on a sample of $Ba[OB(Mes)_2]_2$ by a combustion technique. Carbon dioxide and water vapor are collected during this technique to determine the amounts of carbon and hydrogen in the sample. The expected percentages of carbon and hydrogen were 64.75% and 6.66%, respectively. The experimental results were higher. Elemental analysis determined that the percentage of carbon was 66.57%. The percentage of hydrogen was determined to be 7.22%. A small amount of unreacted dimesitylborinic acid or residual solvent can account for these higher values.

3.1.6 TGA and DSC of $Ba[OB(Mes)_2]_2$

Thermogravimetric analysis (TGA) was performed on $Ba[OB(Mes)_2]_2$ under nitrogen. The temperature was raised to 700 °C at a rate of 10 °C/min. Figure 12 shows the percent weight loss for the sample as a function of temperature. At 700 °C all that remains is roughly 30% of the original mass. Since the mesityl groups in the sample make up 71.4 % of the mass, it is concluded that these groups are no longer present. The molecular weight of $Ba[OB(Mes)_2]_2$ is equal to 667.69 grams/mol. The 4 mesityl groups in the compound have a molecular weight of 476.74 grams/mol accounting for 71.4 % of the overall mass.

Differential Scanning Calorimetry (DSC) was performed, but only to 160 °C (See Figure 13). Any unreacted dimesitylborinic acid will become volatile above this

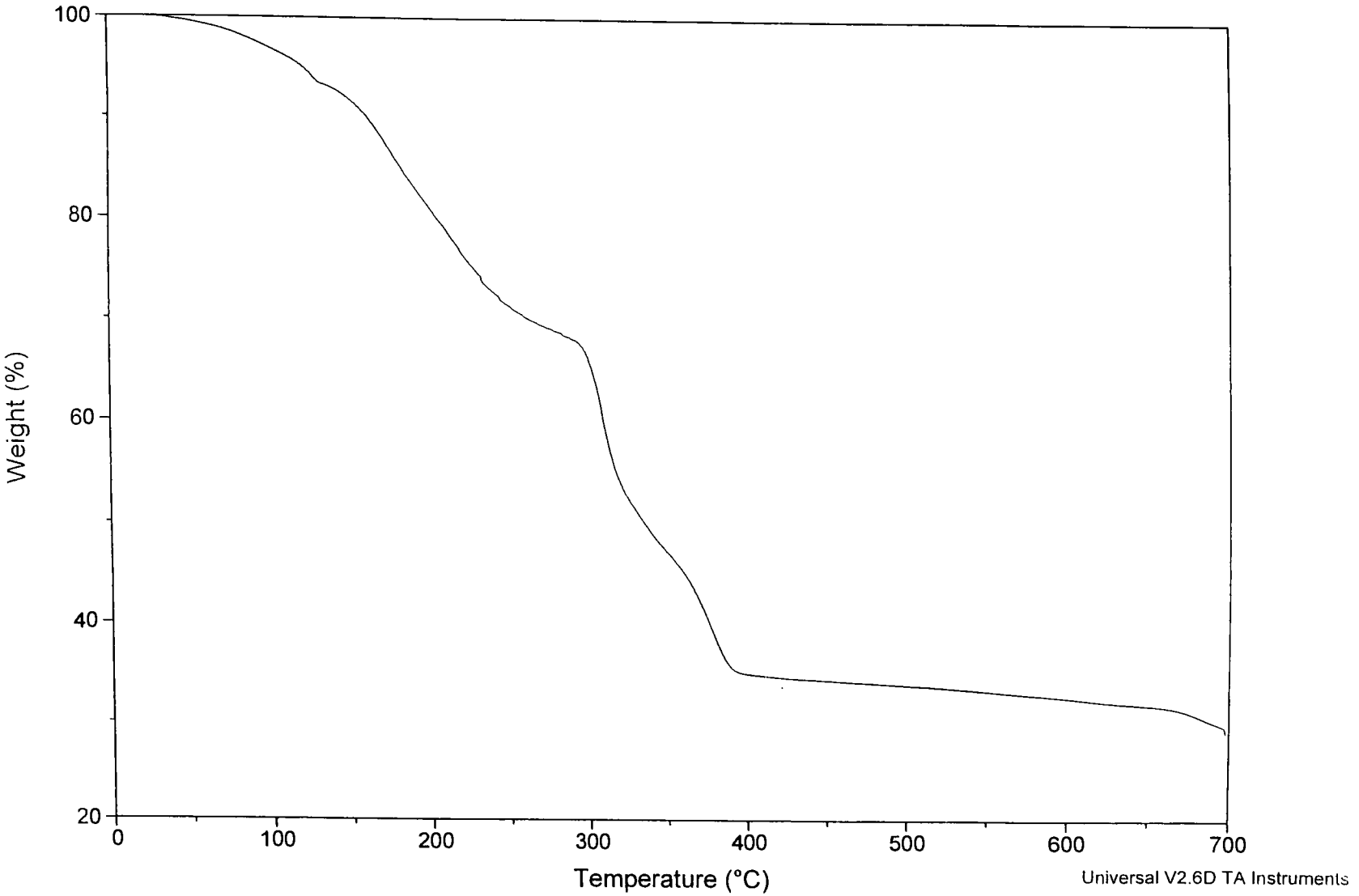


Figure 12. TGA Curve for $Ba[OB(Mes)_2]_2$

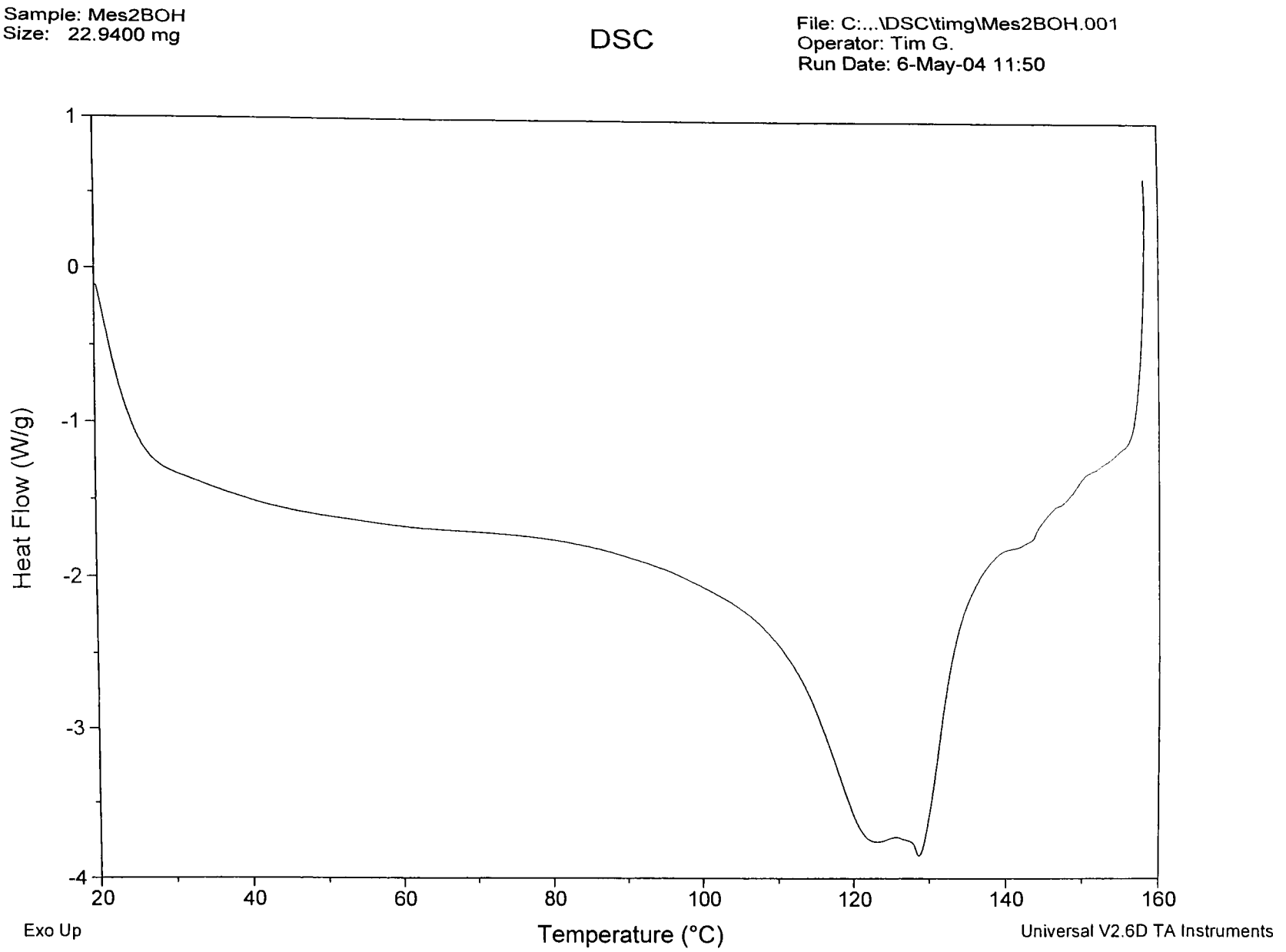


Figure 13. DSC Curve for $Ba[OB(Mes)_2]_2$

temperature and will deposit on the chamber walls causing instrument problems. The initial endotherm could be a result of the removal of residual solvents. Since weight loss continues above 100 °C, the samples dried for elemental analysis should be dried over a higher boiling solvent than water.

3.2 Characterization of Barium (Crown Ether) Cyclotriboroxane Precursor

The barium (crown ether) cyclotriboroxane precursor, prepared from 2,4,6-triethoxycyclotriboroxane and barium (crown ether) ethoxide, was characterized along with the two reactants used to make the precursor. Various techniques such as IR spectroscopy, NMR, TGA, DSC, and elemental analysis were applied.

3.2.1 Infrared Spectroscopy of 2,4,6-Triethoxycyclotriboroxane

The infrared spectrum of 2,4,6-triethoxycyclotriboroxane, sampled as a liquid between two KBr salt plates, was recorded. The IR peaks reported in the literature are as follows [17]:

1521 sh, 1495 vs, 1433 vs, 1383 vs, 1341 vs, 1289 s, 1215 w, ~1164 w, 1107 s, 1080 s, ~1055 sh, ~961 w, ~824 w, 804 w, ~736 sh, 722 s

(vs=very strong, s=strong, m=medium, w=weak, sh=shoulder)

Peaks with strong absorptions near 720 and 735 cm^{-1} are representative of metaboric esters as reported by Lappert [17]. Bands at 1080 and 1383 cm^{-1} represent the stretching of B-O and C-O bonds in ethyl metaborate [18]. Figures 14 and 15 show the IR spectra of non-purified and purified 2,4,6-triethoxycyclotriboroxane, respectively. As can be seen from the spectra, the weaker peaks in the purified sample are more highly resolved. The labeled peaks for the 2,4,6-triethoxycyclotriboroxane samples closely match those reported in the literature, with the purified sample peaks being slightly closer. Figure 16 shows the IR spectrum of triethylborate, one of the starting materials. The only major difference between this sample and the product is the lack of peaks at 720 and 735 cm^{-1}. Figure 17 shows an overlay of the three plots.

3.2.2 Proton NMR of Barium (Crown Ether) Ethoxide

A sample of barium (crown ether) ethoxide was dried in the Abderhalden apparatus at 100 °C and analyzed by proton NMR in deuterated methanol. Figure 18 shows the resulting NMR spectrum. The peaks located at 1.8 and 3.7 ppm are due to the deuterated methanol (see Figure 19). The peaks at 1.1 and 3.5 ppm are due to the protons in the ethoxide group. The ratio of the integrated peak heights for the ethoxide protons was found to be 3:5. These measurements are close to the expected ratio of 4:6. The peak at 3.2 ppm is attributed to the methylene protons in 18-crown-6. Crown ether contains 24 protons. Therefore, the integrated peak height for 18-crown-6 should be four times as large as the ethoxide peak at 1.1 ppm since this peak is attributed to 6 protons. However, the height of the integrated peak was measured to be only three times as large. It is

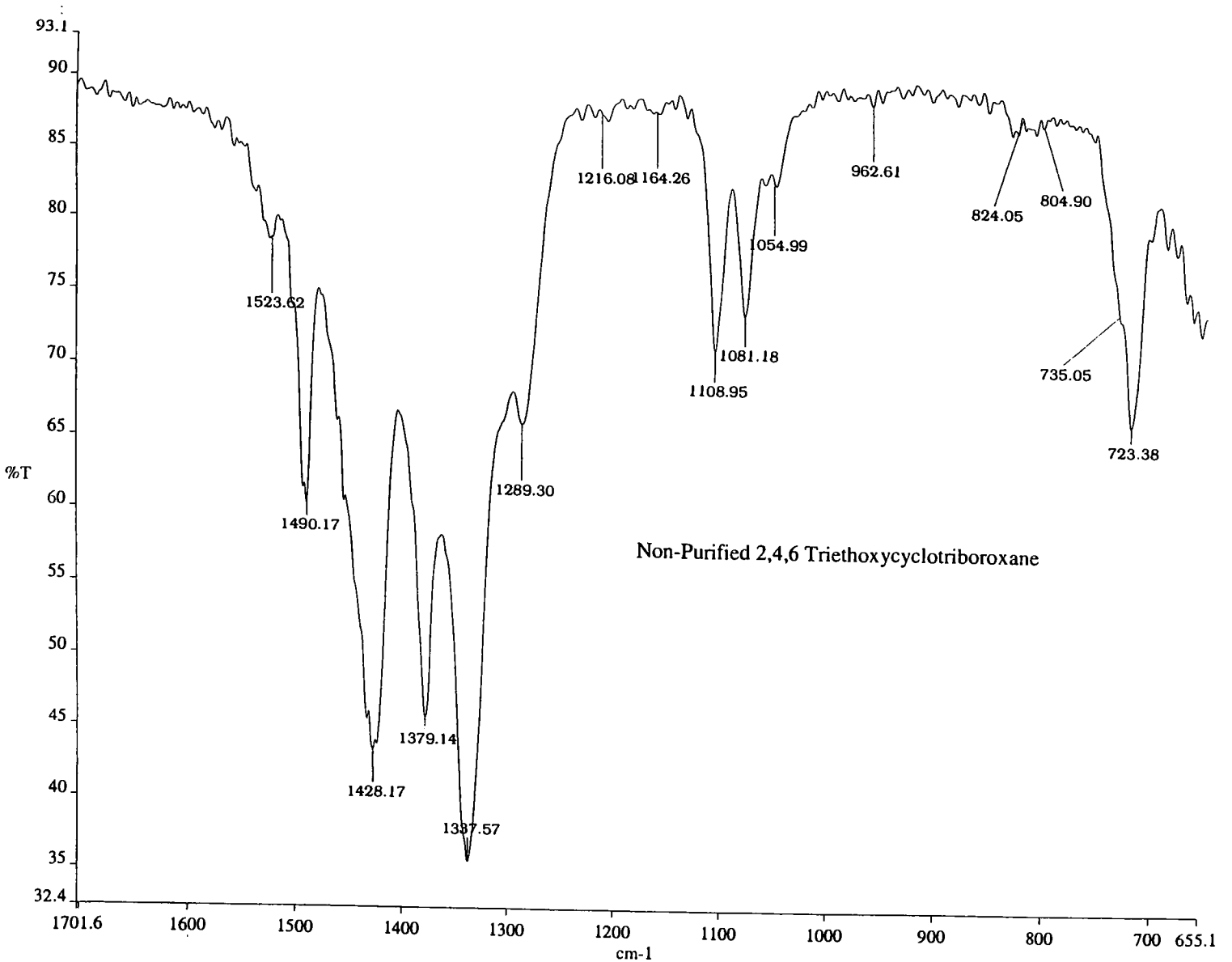


Figure 14. IR Spectrum for Non-Purified 2,4,6-Triethoxycyclotriboroxane

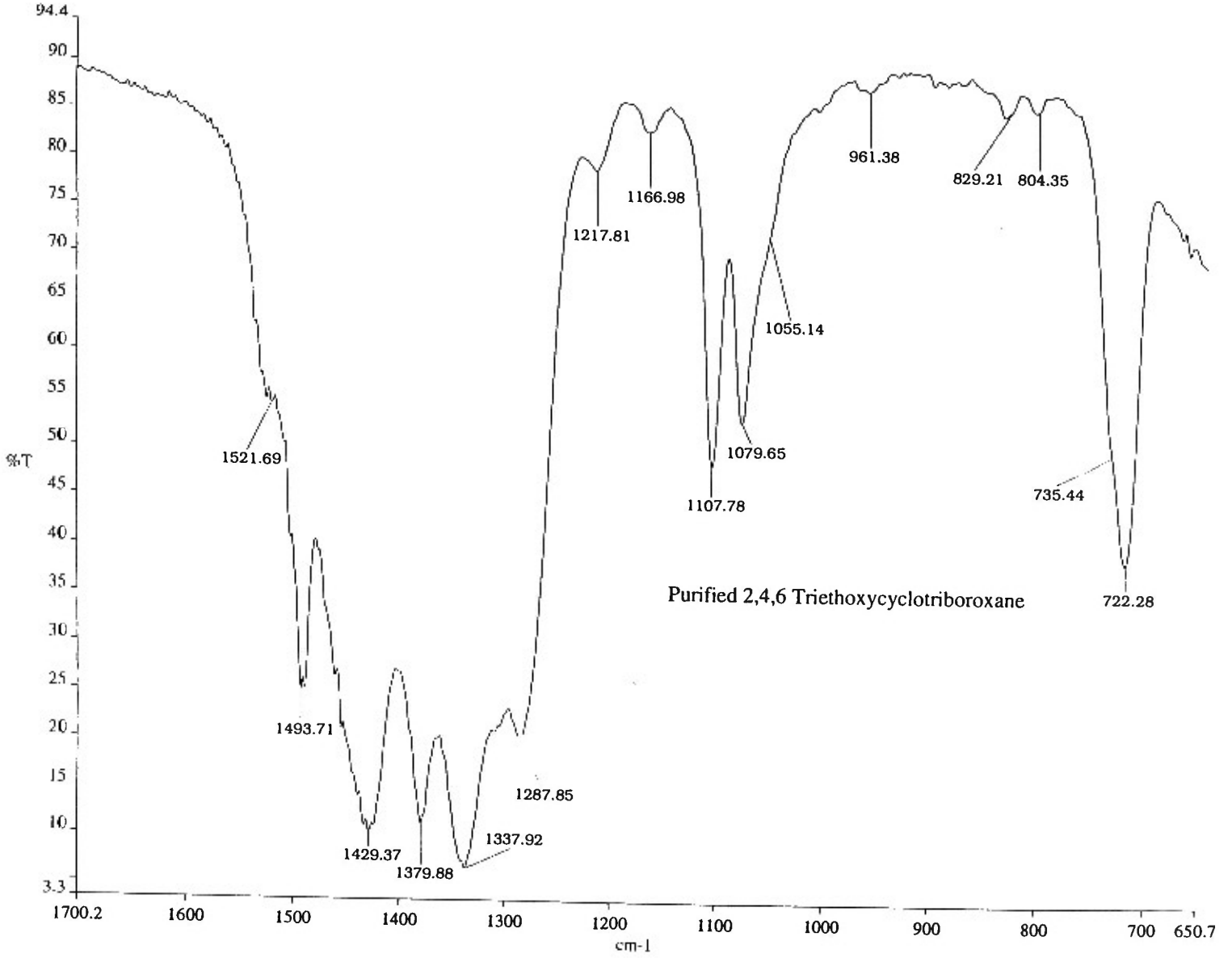


Figure 15. IR Spectrum for Purified 2,4,6-Triethoxycyclotriboroxane

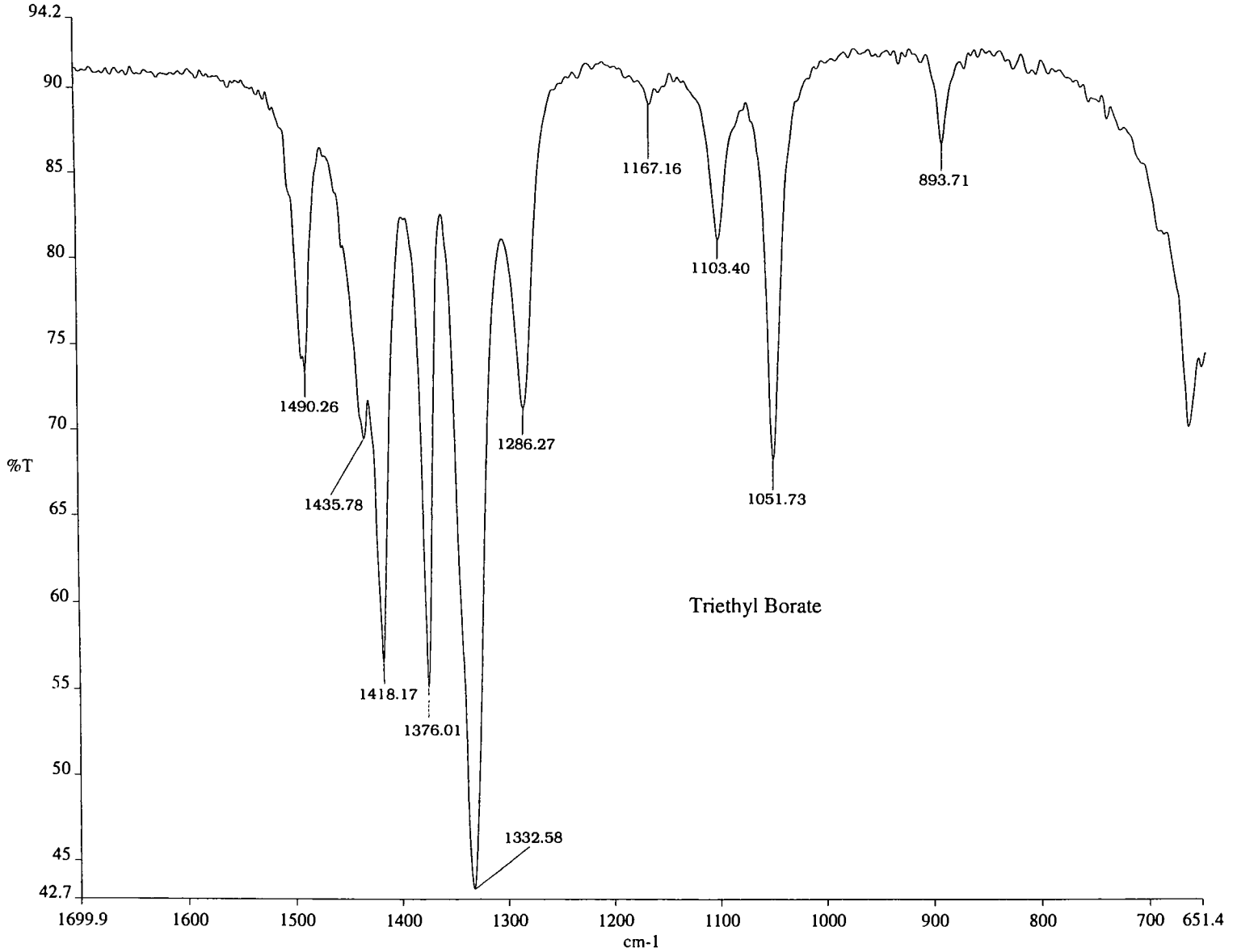


Figure 16. IR Spectrum for Triethyl Borate

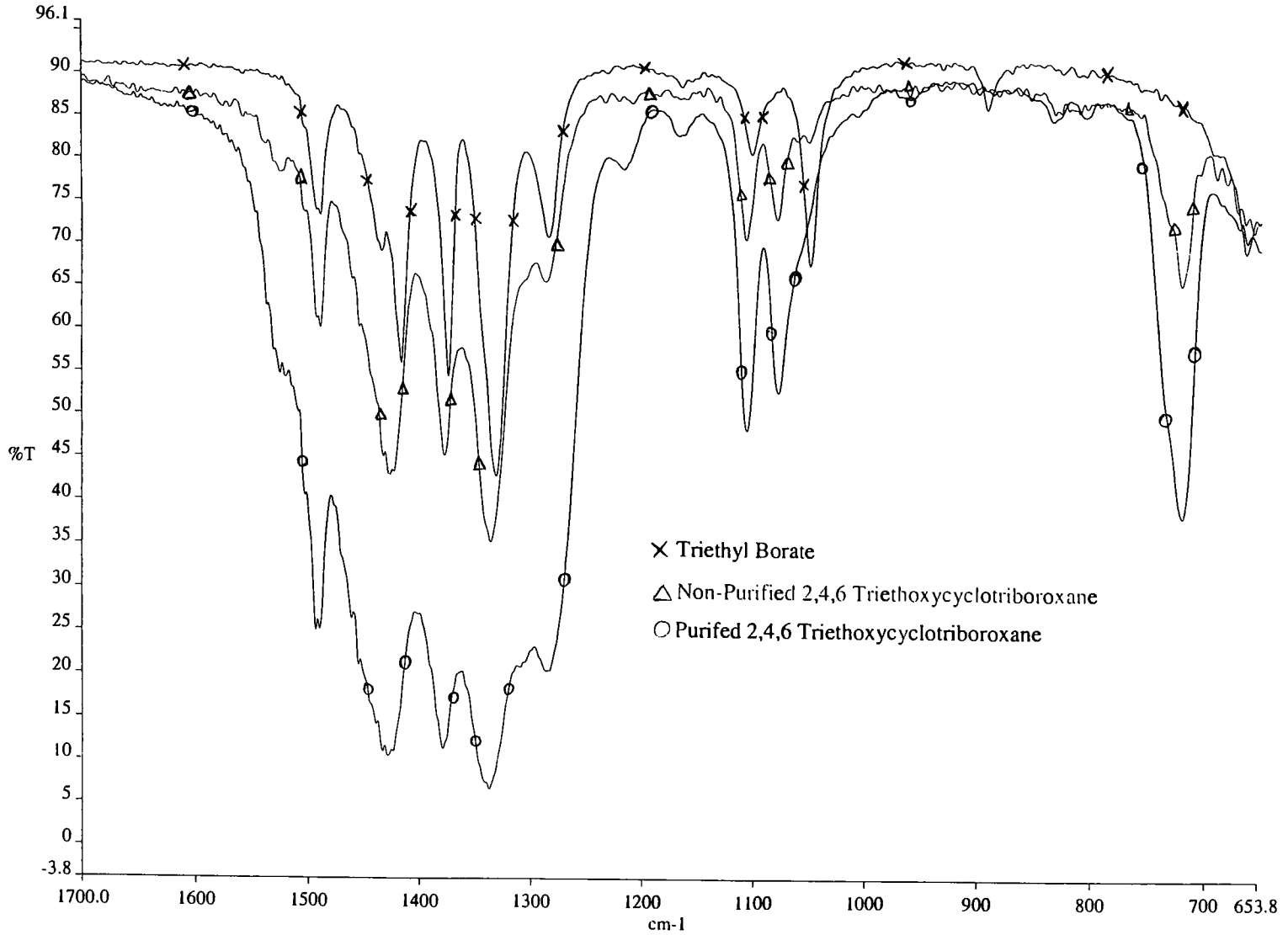
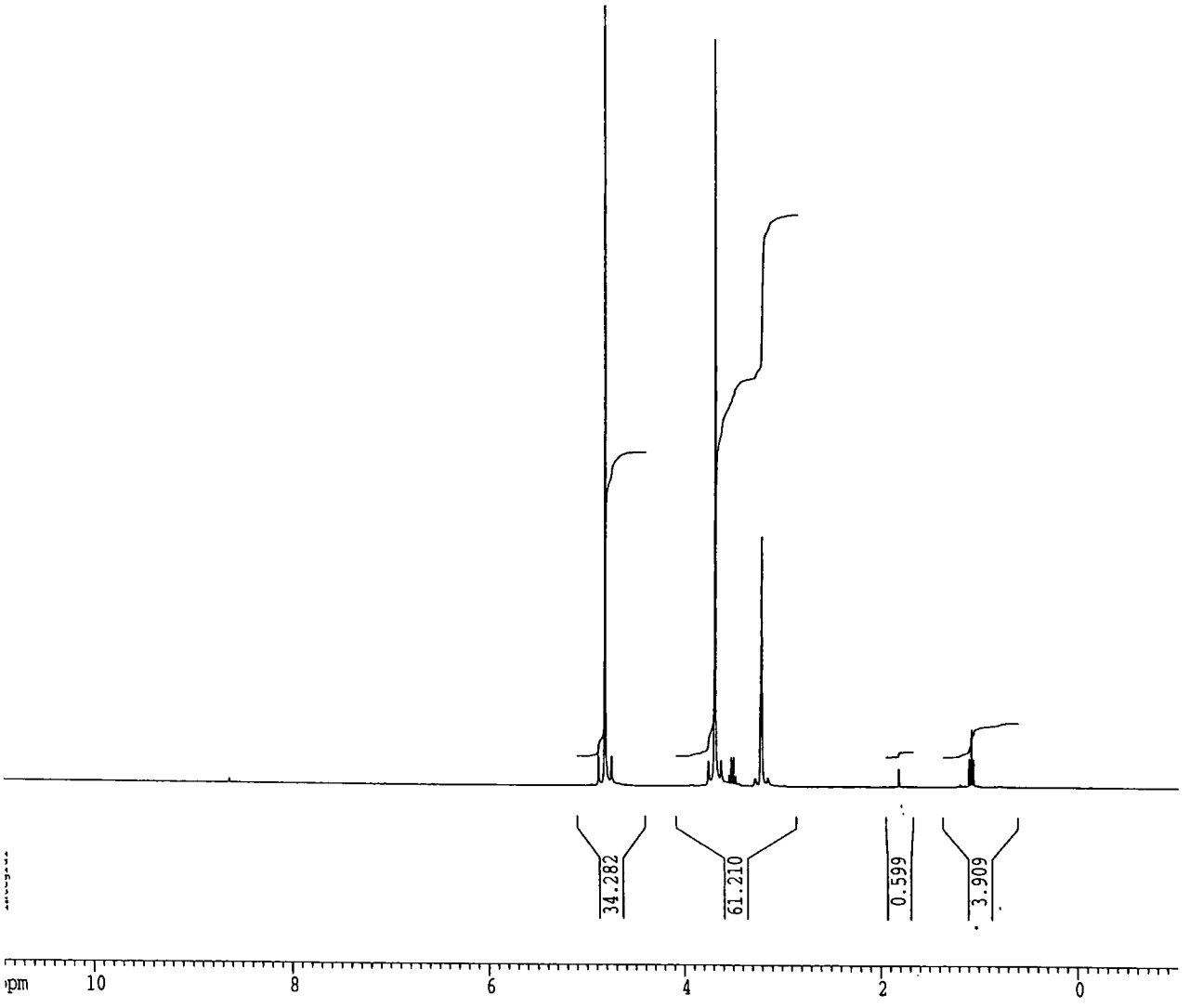


Figure 17. Overlay of IR Spectra for 2,4,6-Triethoxycyclotriboroxane and Triethyl Borate

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PROCNO                  1

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PULPROG             zg30
TD                 65536
SOLVENT             MeOH
NS                    16
DS                     2
SWH             6172.839 Hz
FIDRES          0.094190 Hz
AQ              5.3084660 sec
RG                 456.1
DW                81.000 usec
DE                 6.00 usec
TE                300.0 K
D1             1.00000000 sec

============ CHANNEL f1 ============
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P1                   9.50 usec
PL1                 -3.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
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WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
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F1                3301.43 Hz
F2P                -1.000 ppm
F2                -300.13 Hz
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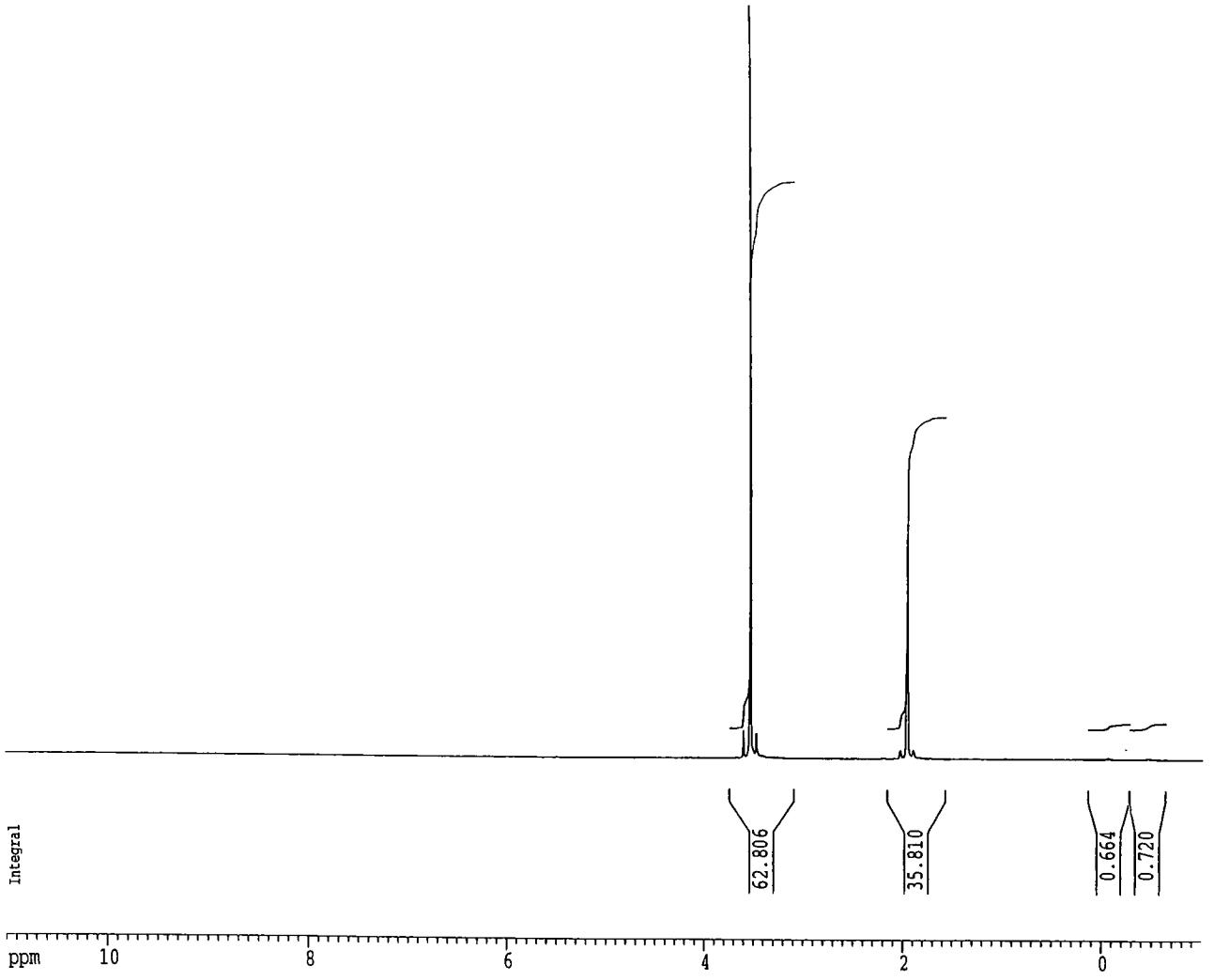
HZCM          180.07802 Hz/cm
```

Figure 18. Proton NMR of Barium (Crown Ether) Ethoxide in Deuterated Methanol

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SOLVENT             MeOH
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DS                     2
SWH             6172.839 Hz
FIDRES          0.094190 Hz
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RG                 645.1
DW                81.000 usec
DE                 6.00 usec
TE                300.0 K
D1             1.00000000 sec

============ CHANNEL f1 ============
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PL1                 -3.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
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SF           300.1299436 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
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F1P                11.000 ppm
F1                3301.43 Hz
F2P                -1.000 ppm
F2                -300.13 Hz
PPMCM             0.60000 ppm/cm
HZCM             180.07797 Hz/cm
```

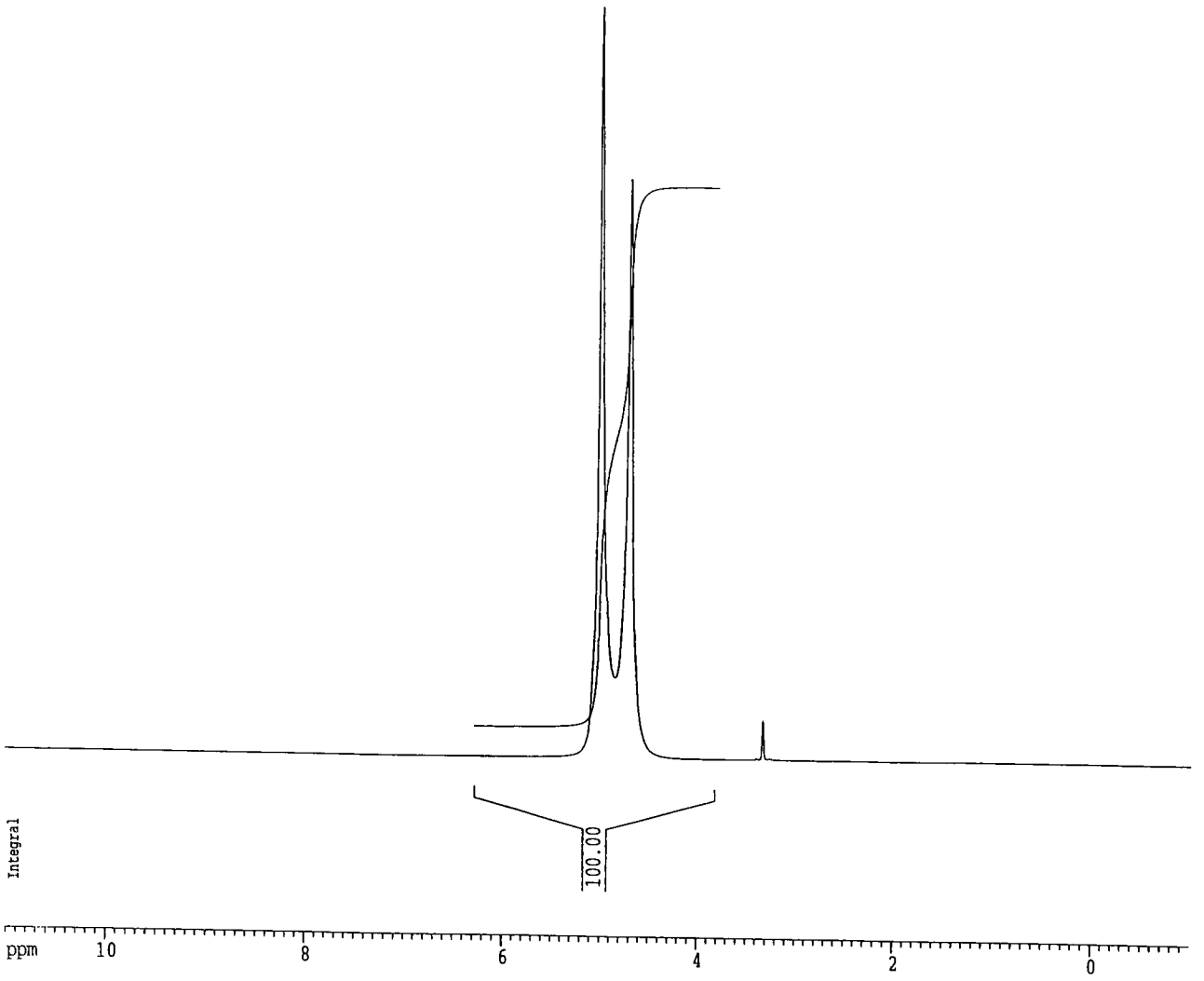
Figure 19. Proton NMR of Deuterated Methanol

determined that the amount of crown ether in the sample is less than expected. It is possible that a portion of the crown ether is lost to sublimation during the drying process. A similar explanation seems appropriate for barium (crown ether) cyclotriboroxane (vide infra). The peak at 4.8 ppm is due water in the deuterated solvent (See Figure 20).

3.2.3 IR Spectroscopy of Crown Ether and Barium (Crown Ether) Ethoxide

Figure 21 shows the IR spectrum of 18-crown-6. The spectrum was taken for the cyclic polyether as received from the vendor. C-O-C stretching vibrations are expected to be found between 1270 and 1030 cm^{-1} [18]. In this region six medium to small bands are observed. The bands observed at high wavenumbers, 2800-2950 cm^{-1}, can be attributed to aliphatic C-H stretching vibrations. The remaining peaks can be accounted for by C-C and crown ether ring vibrations. Figure 22 shows the IR spectrum for barium (crown ether) ethoxide. Of the six bands in the 1270 to 1030 cm^{-1} range, the peak at 1122.39 cm^{-1} appears to shift and become a shoulder. This is consistent with what is expected for the C-O-C vibration upon complexation. Peaks located at 2787.13, 2750.20, 2673.33 and 2571.99 cm^{-1} can be accounted for by the O-Et stretching vibrations for barium ethoxide. Figure 23 shows the presence of these peaks in a similar compound, sodium ethoxide. Neat samples were used for these three IR spectra.

3.2.4 TGA and DSC of Barium (Crown Ether) Ethoxide

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DS                     2
SWH           6172.839 Hz
FIDRES        0.094190 Hz
AQ            5.3084660 sec
RG                    32
DW              81.000 usec
DE               6.00 usec
TE              300.0 K
D1            1.00000000 sec

============ CHANNEL f1 ============
NUC1                  1H
P1                 9.50 usec
PL1               -3.00 dB
SFO1        300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF          300.1300000 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                 1.00

1D NMR plot parameters
CX                20.00 cm
F1P              11.000 ppm
F1              3301.43 Hz
F2P              -1.000 ppm
F2              -300.13 Hz
PPMCM           0.60000 ppm/cm
HZCM          180.07800 Hz/cm
```

Figure 20. Proton NMR of Water in Deuterated Methanol

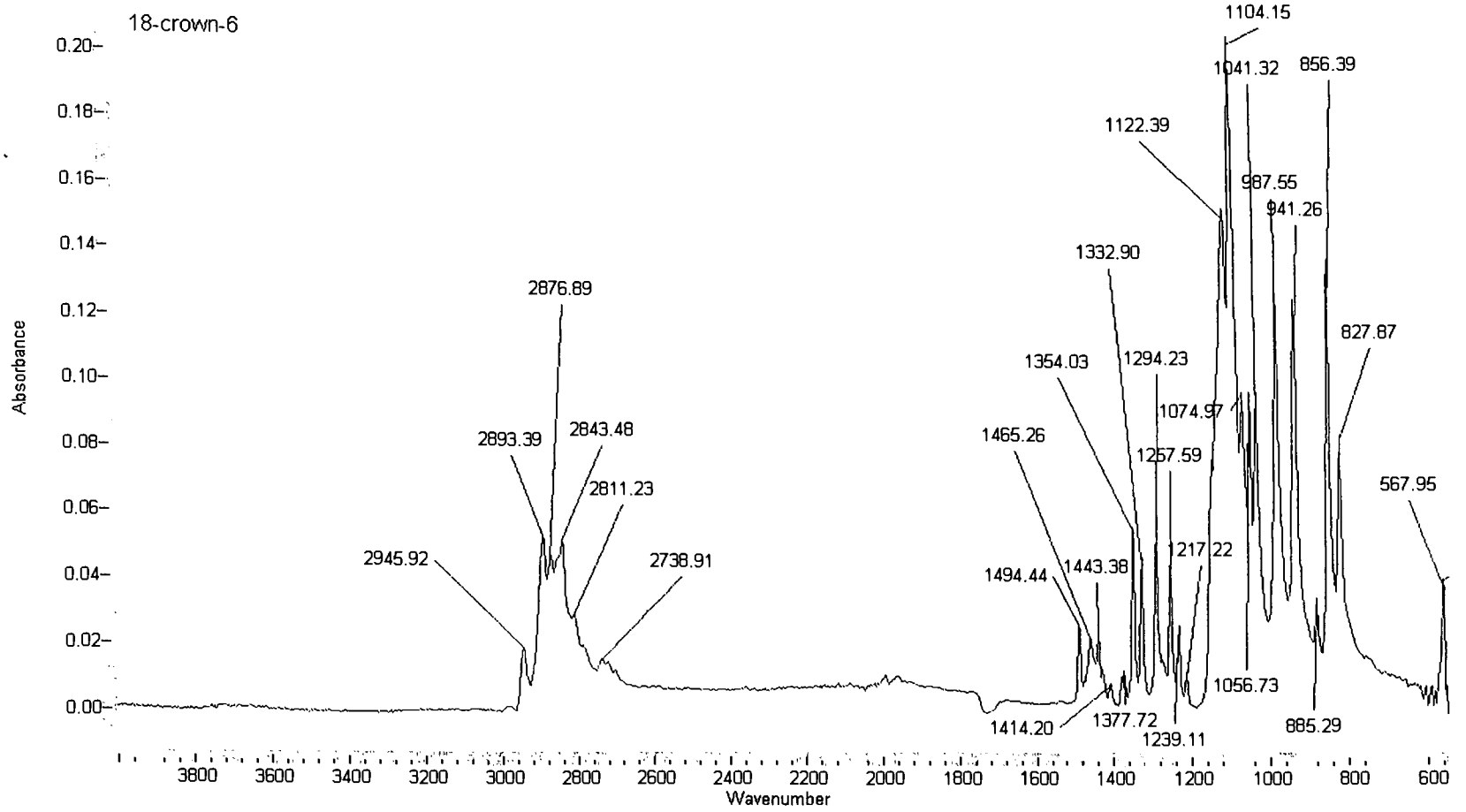


Figure 21. IR Spectrum of 18-Crown-6

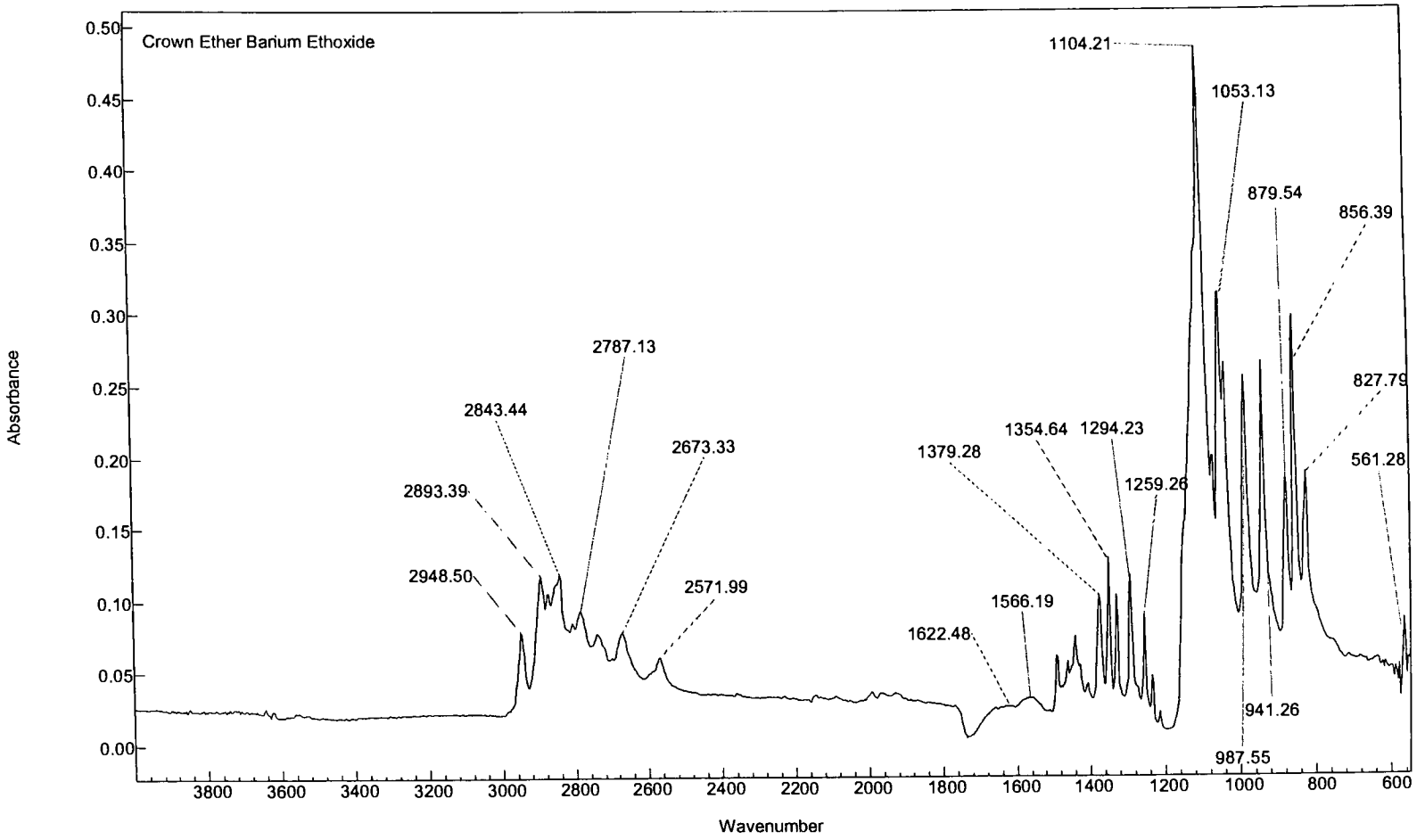


Figure 22. IR Spectrum of Barium (Crown Ether) Ethoxide

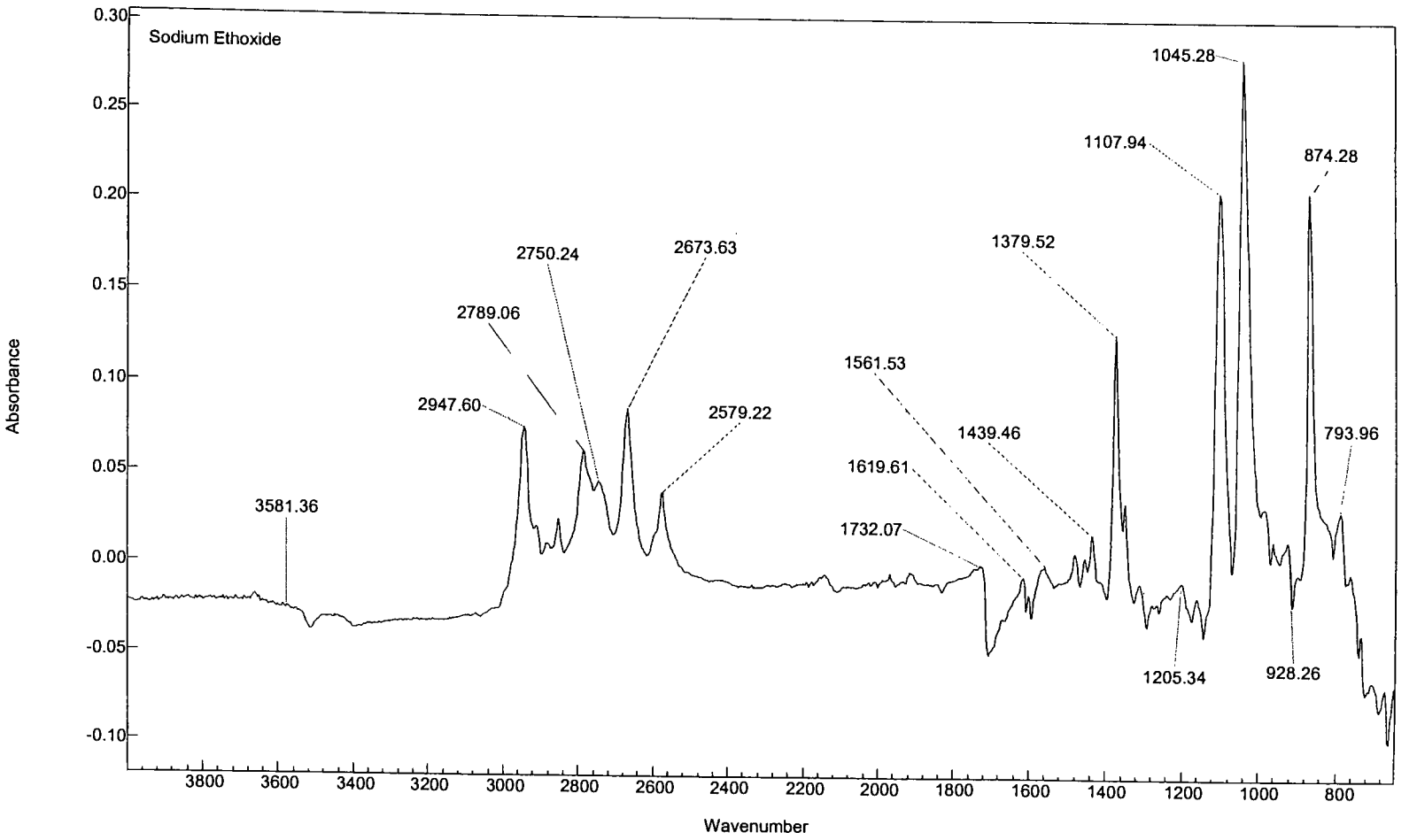


Figure 23. IR Spectrum for Sodium Ethoxide

TGA was performed on a sample of barium (crown ether) ethoxide at a heating rate of 10°C/min up to 700°C. The test was performed under nitrogen. The plot for this experiment is given in Figure 24. From the onset weight loss is occurring. At temperatures less than 100°C some of the residual solvent is removed. From 140°C to approximately 360°C a major weight loss occurs. This weight loss can be attributed to the removal of crown ether from the compound. Barium (crown ether) ethoxide contains crown ether as 54% of its mass. The molecular weight of barium (crown ether) ethoxide is 491.77 g/mol. The molecular weight of crown ether is 264.32 g/mol or 54 % of the above compound's molecular weight. What remains after heating the sample to 360°C is approximately 39% of the original mass. If the removal of residual solvents is taken into account this weight percent is consistent with the full removal of crown ether from the sample. A majority of the crown ether is removed by 240°C. A much smaller weight loss event takes place from 240°C to nearly 370°C. If CO_2 is generated during the weight loss up to 240 °C, formation and subsequent decomposition of barium ethyl carbonate could explain the smaller weight loss. This weight loss is much too small to be a conversion of $Ba(OEt)_2$ to BaO or BaO_2. Figure 25 is a DSC scan taken of the same material. The heating rate was set at 10°C/min up to 600°C. This test was also performed under nitrogen. The endotherm that is present at 50°C is probably due to absorbed water in the DSC chamber. At temperatures around 100°C the residual solvent is being removed. As temperature is increased the heat flow continues to be endothermic as crown ether evaporates. At 250 °C an exothermic event takes place as the crown ether is decomposed. Carbon dioxide from the decomposition may react with barium ethoxide to form barium ethyl carbonate. Another exothermic event at 290°C could be due to a

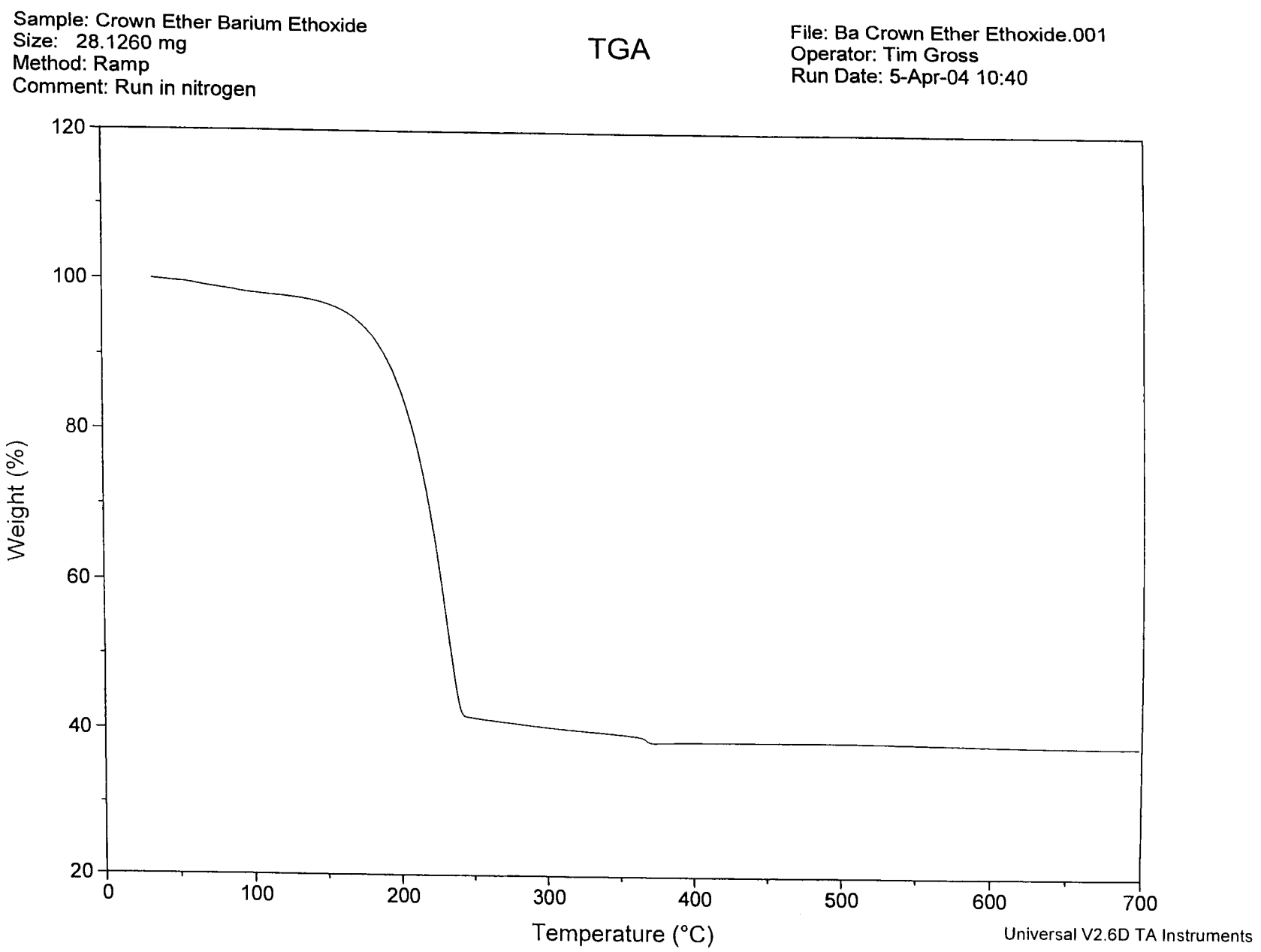


Figure 24. TGA Curve for Barium (Crown Ether) Ethoxide

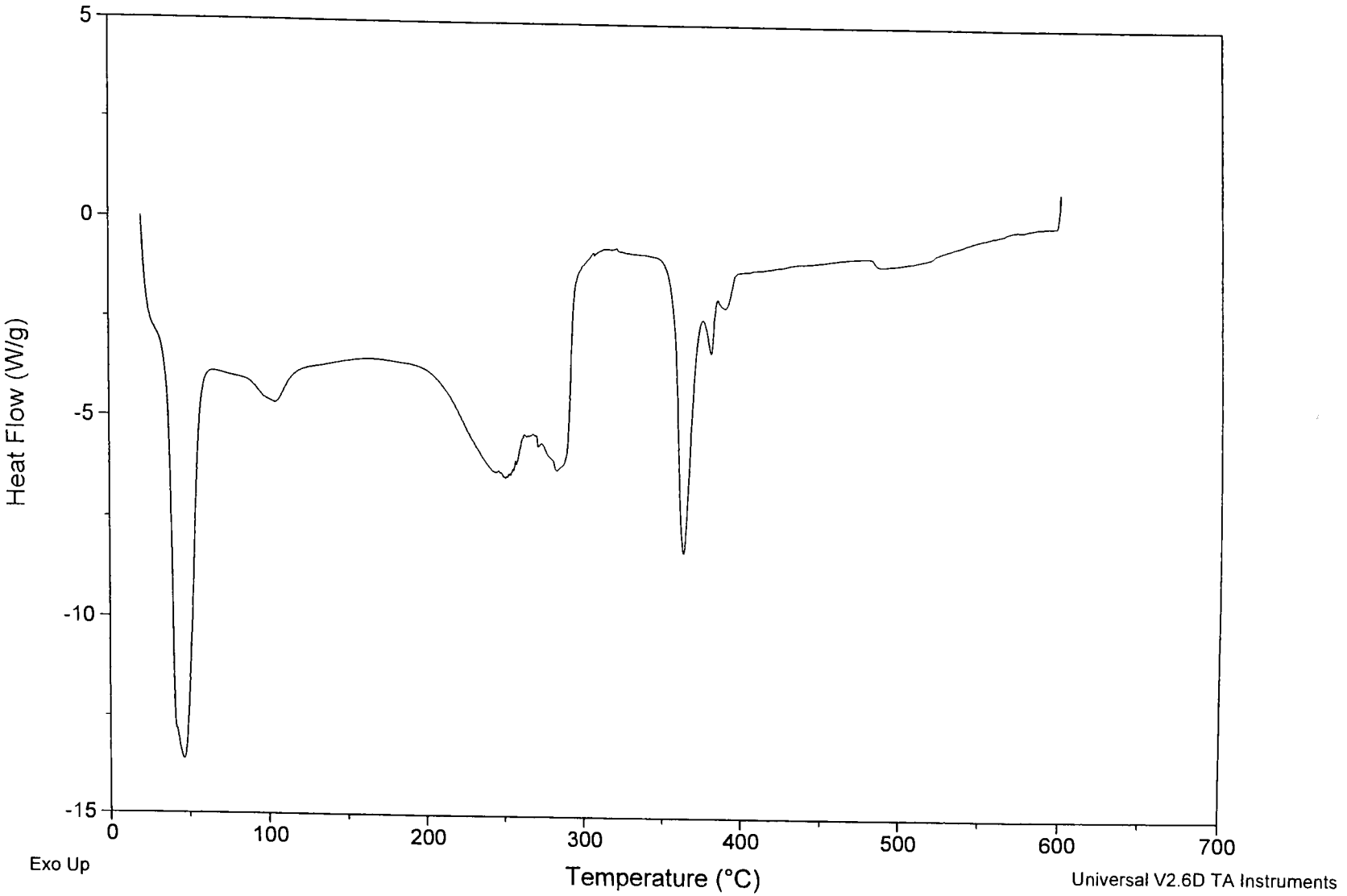


Figure 25. DSC Curve for Barium (Crown Ether) Ethoxide

spatial rearrangement as gaps left from the crown ether are filled. A set of endothermic peaks are observed between 350 and 400°C. These endothermic peaks may be due to the decomposition of barium ethyl carbonate.

3.2.5 IR Spectroscopy of Barium (Crown Ether) Cyclotriboroxane Precursor

IR spectroscopy was performed on barium (crown ether) cyclotriboroxane precursor powders. Hydrolyzed and non-hydrolyzed powders were examined. Figure 26 shows the IR spectrum of non-hydrolyzed precursor powder. The IR spectrum closely matches the IR spectrum for 18-crown-6 shown in Figure 21. Additional peaks at 713.85 and 746.68 cm^{-1} are representative of the metaboric ester [17]. A band should be present at 1383 cm^{-1} for B-O stretching within the anionic ring [18]. Its presence cannot be determined due to overlapping of the crown ether bands. The spectrum of the hydrolyzed precursor is shown in Figure 27. Hydrolysis is performed on the precursor to aid in the removal of organics during the heat treatment process. Again, nearly all the bands can be accounted for by the crown ether and a band is present at 711.73 cm^{-1} that likely arises from the metaboric ester. It should be noted that ethoxide peaks are not present in either of these spectra, as expected.

3.2.6 Elemental Analysis of Barium (Crown Ether) Cyclotriboroxane Precursors

Elemental analysis was performed on the non-hydrolyzed and hydrolyzed barium (crown ether) cyclotriboroxane precursors. The non-hydrolyzed precursor is expected to

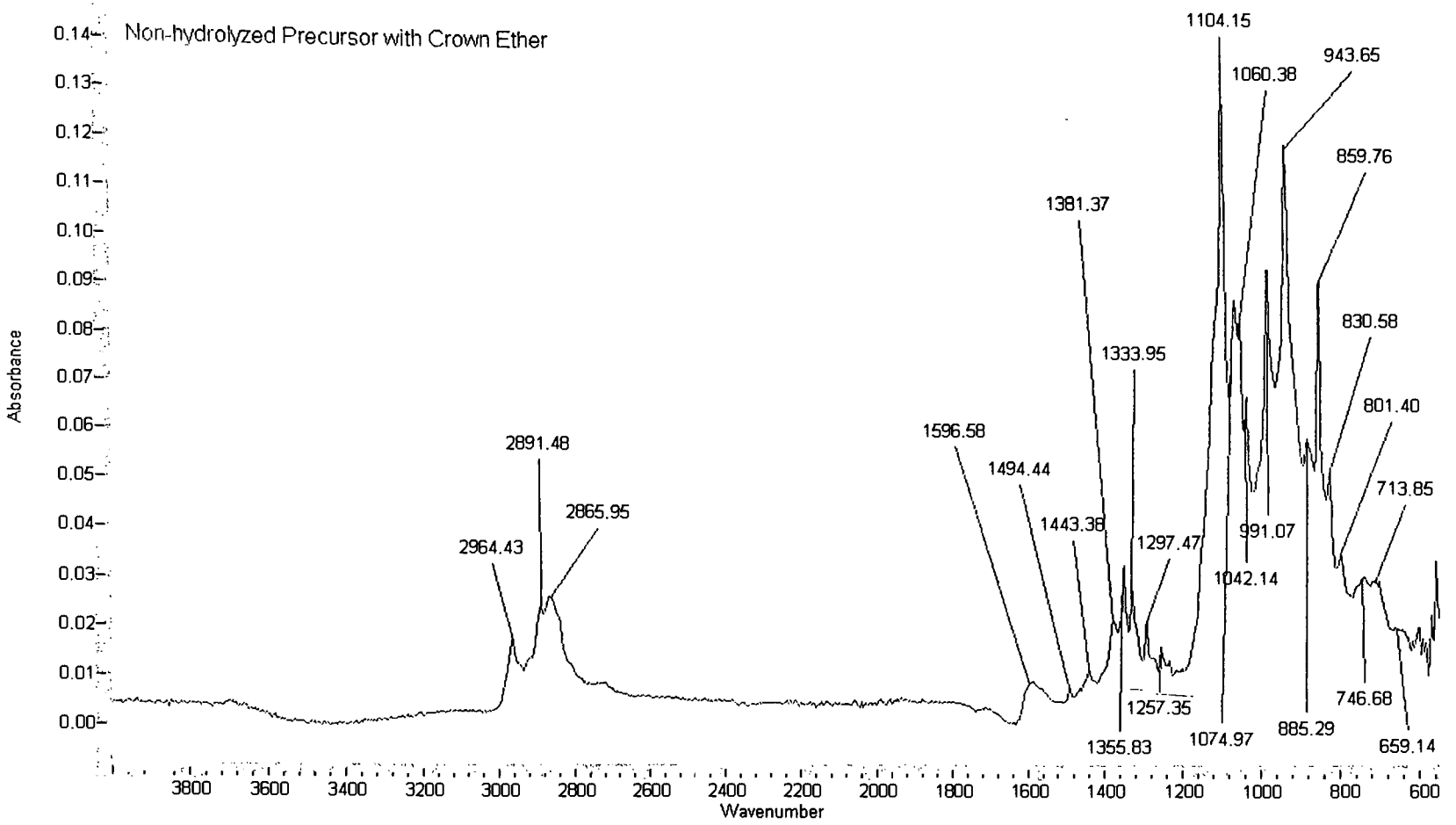


Figure 26. IR Spectrum for Non-Hydrolyzed Barium (Crown Ether) Cyclotriboroxane

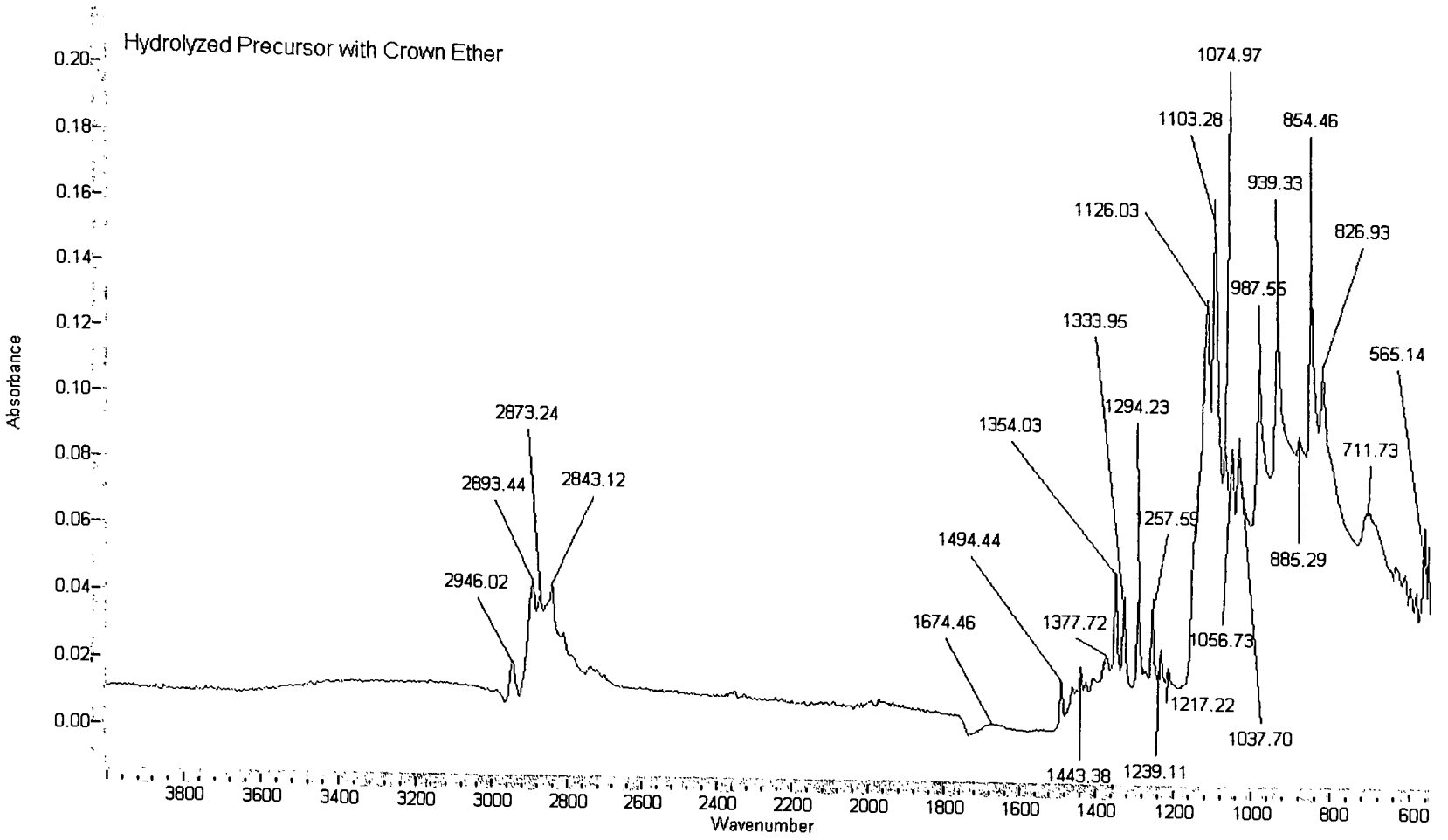


Figure 27. IR Spectrum for Hydrolyzed Barium (Crown Ether) Cyclotriboroxane

form $Ba_3B_6O_{12}$ including three crown ethers, see Figure 2. This compound will contain 29.58% carbon and 4.96% hydrogen of its total mass. The elemental analysis of this sample revealed that the precursor consisted of 27.86% carbon and 4.91% hydrogen. It is possible that the sample contains some residual solvent or is non-stoichiometric in crown ether. If the compound where composed of $Ba_3B_6O_{12}$ plus two crown ethers then the compound would contain carbon as 24.07% and hydrogen as 4.04% of its mass. If 68.80% of the precursor contains 3 crown ethers while the remaining portion only contains 2 crown ethers then the elemental analysis for carbon is accurate.

$$0.688(29.58) + 0.312(24.07) = 27.86\% \text{ Carbon}$$

$$0.688(4.96) + 0.312(4.04) = 4.67\% \text{ Hydrogen}$$

This elemental analysis for hydrogen is within experimental error. This supports the interpretation that the sample is a mixture of $Ba_3(CE)_2B_6O_{12}$ and $Ba_3(CE)_3B_6O_{12}$.

The hydrolyzed precursor is expected to contain 2 hydrolyzed borate rings, 3 $Ba(OH)_2$ molecules, and 3 crown ethers. This mixture of compounds is expected to contain 27.54% carbon and 5.39% hydrogen. The elemental analysis revealed 23.84% carbon and 4.34% hydrogen. In this case it is possible that the hydrolysis step removes more of the crown ether in the sample, thus lowering the percentages of carbon and hydrogen further vs. the unhydrolyzed sample. If the sample contains 2 crown ethers instead of 3, the percentages of carbon and hydrogen are expected to be 22.08 % and 4.63 %, respectively. If 32.2 % of the sample contains 3 crown ethers and 67.8 % of the sample contains 2 crown ethers then the elemental analysis for the carbon is correct.

$$0.322(27.54) + 0.678(22.08) = 23.84\ \% \text{ Carbon}$$

$$0.322(5.39) + 0.678(4.63) = 4.87\ \% \text{ Hydrogen}$$

In this case, the percentage of hydrogen is incorrect when only considering a loss of crown ether. Therefore, it is likely that residual solvent is having some effect on the elemental analysis. However, the loss of crown ether must have taken place to account for the low percentage of carbon in the elemental analysis. It is possible that crown ether is removed from the sample in the Abderhalden during drying.

3.2.7 TGA and DSC of Barium (Crown Ether) Cyclotriboroxane Precursor Powders

TGA was performed under nitrogen at a heating rate of 10 °C/min up to 700 °C. The curve for the non-hydrolyzed barium (crown ether) cyclotriboroxane precursor is given in Figure 28. From the onset of heating up to 300 °C a major weight loss is occurring. For the non-hydrolyzed precursor it expected that crown ether consists of 54% of the precursor mass. If the removal of residual solvent is responsible for the mass loss below 50 °C, the mass loss by 300 °C can be attributed to a 100% removal of crown ether.

The DSC for the non-hydrolyzed precursor is given in Figure 29. This analysis was performed under nitrogen up to 600 °C at 10 °C/min. The initial endotherm is most likely an artifact. As the temperature is increased up to 300 °C the residual solvent and crown ether are removed from the sample. The exothermic event at 300 °C could be caused by a spatial rearrangement as the voids left by the crown ether are filled. The exotherm at 550 °C is the transition of the barium borate to the β phase.

The TGA for the hydrolyzed precursor is shown in Figure 30. The hydrolyzed precursor is expected to contain crown ether as 51% of the overall mass. As the

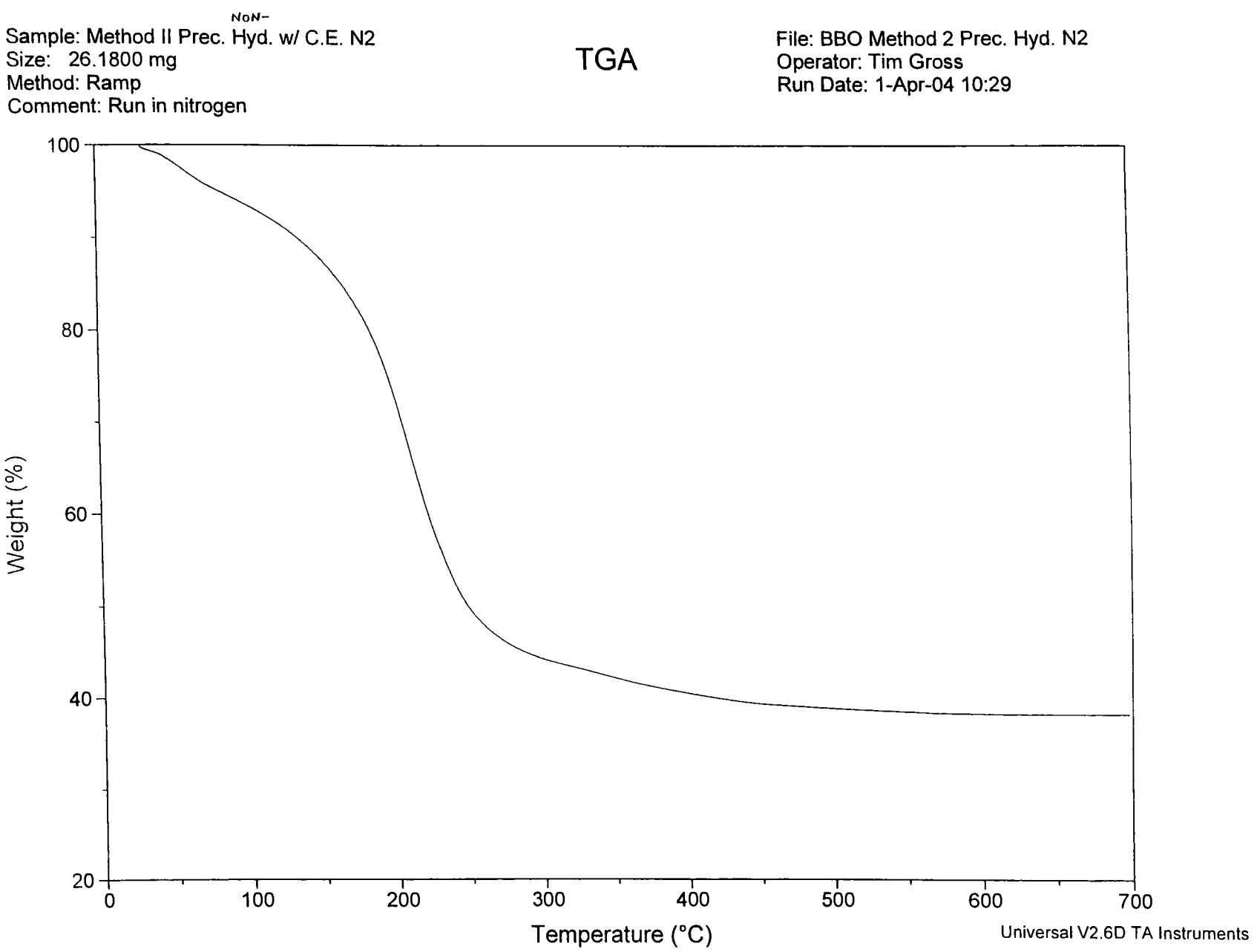


Figure 28. TGA Curve for Non-Hydrolyzed Barium (Crown Ether) Cyclotriboroxane

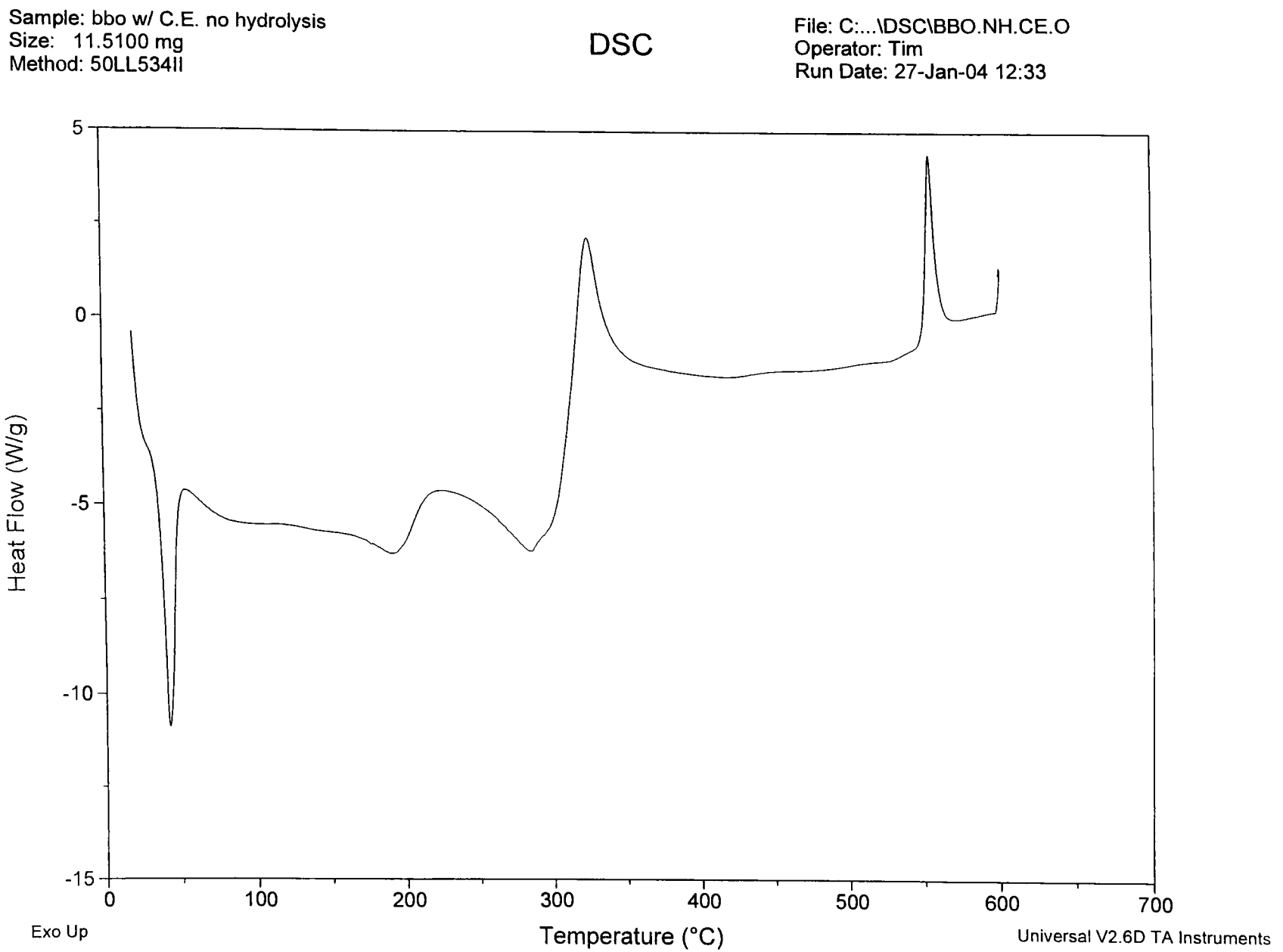


Figure 29. DSC Curve for Non-Hydrolyzed Barium (Crown Ether) Cyclotriboroxane

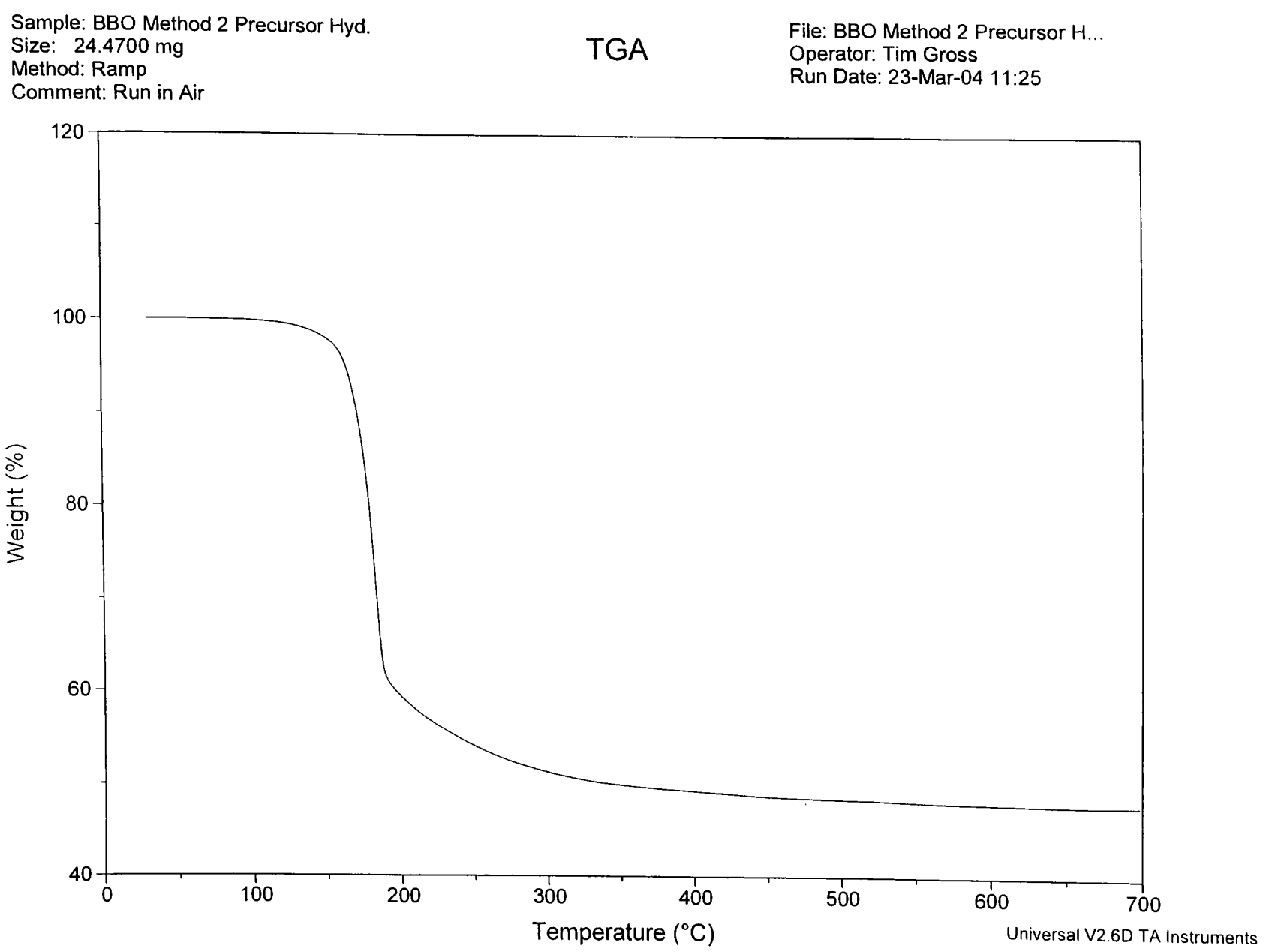


Figure 30. TGA Curve for Hydrolyzed Barium (Crown Ether) Cyclotriboroxane

temperature is raised to 300 °C what remains is just below 50% of the original mass. At this point all of the crown ether has been removed. It is evident by the slope of the curve that the weight loss occurs at a faster rate for the hydrolyzed precursor. This supports the proposal that hydrolysis aids in the removal of organics.

The DSC for the hydrolyzed precursor is given in Figure 31. The initial endotherm is assumed to be an artifact of the instrument. As the temperature is raised to 300 °C the residual solvent and crown ether are removed from the sample. Again, at 300 °C a spatial rearrangement is believed to take place. At approximately 400°C the $Ba(OH)_2$ in the sample forms BaO. This occurrence is supported by Figure 32. At approximately 400 °C the $Ba(OH)_2$ from a sample of $Ba(OH)_2*8H_2O$ is converted to BaO. The DSC for $Ba(OH)_2*8H_2O$ also shows this transition and is given in Figure 33. At approximately 540 °C in Figure 31 the β phase of barium borate is formed as indicated by the exotherm, which closely matches that for the unhydrolyzed barium (crown ether) cyclotriboroxane precursor.

3.2.8 IR Analysis of Barium (Crown Ether) Cyclotriboroxane Precursors at Various Stages of Heat Treatment

IR spectra were recorded for the barium (crown ether) cyclotriboroxane precursors at various stages of heat treatment. Figure 34 shows the spectra for the non-hydrolyzed precursor without any heat, then heated to 150, 280, and 375 °C. These points were chosen to correspond with various points of the DSC curve shown in Figure 28. Figure 21 shows the IR spectrum for 18-crown-6. By comparison it is determined

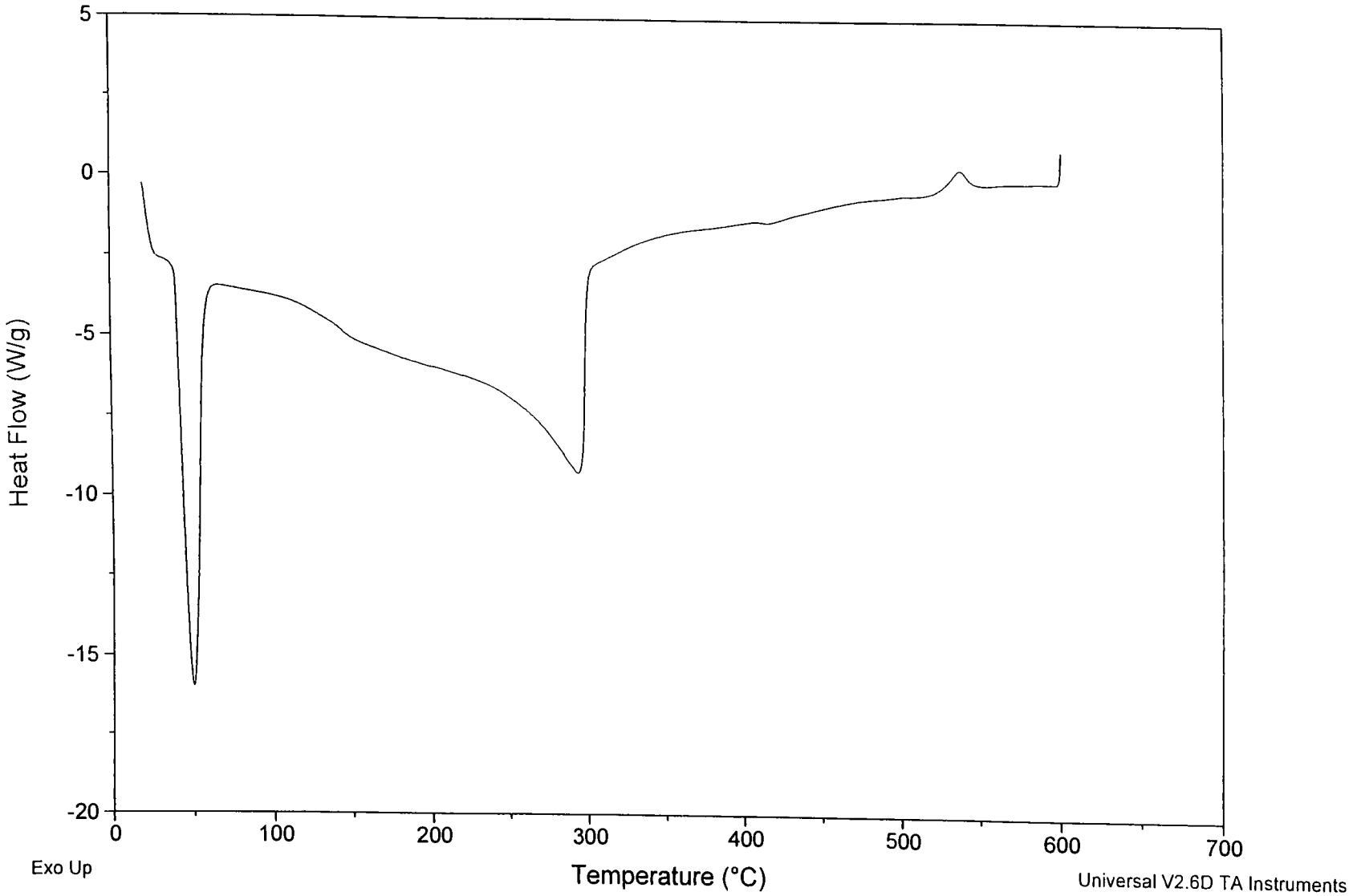


Figure 31. DSC Curve for Hydrolyzed Barium (Crown Ether) Cyclotriboroxane

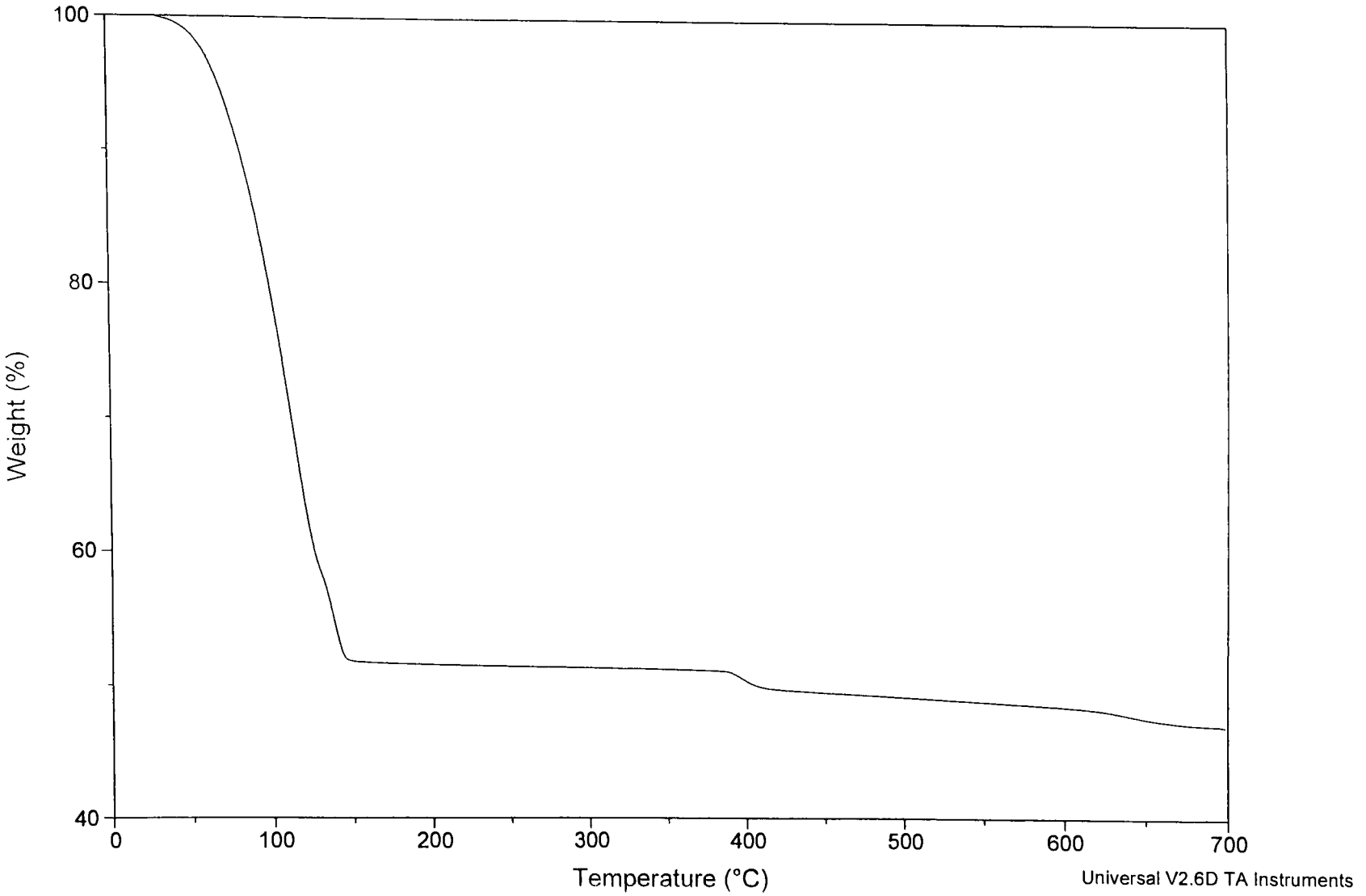


Figure 32. TGA Curve for $Ba(OH)_2*8H_2O$

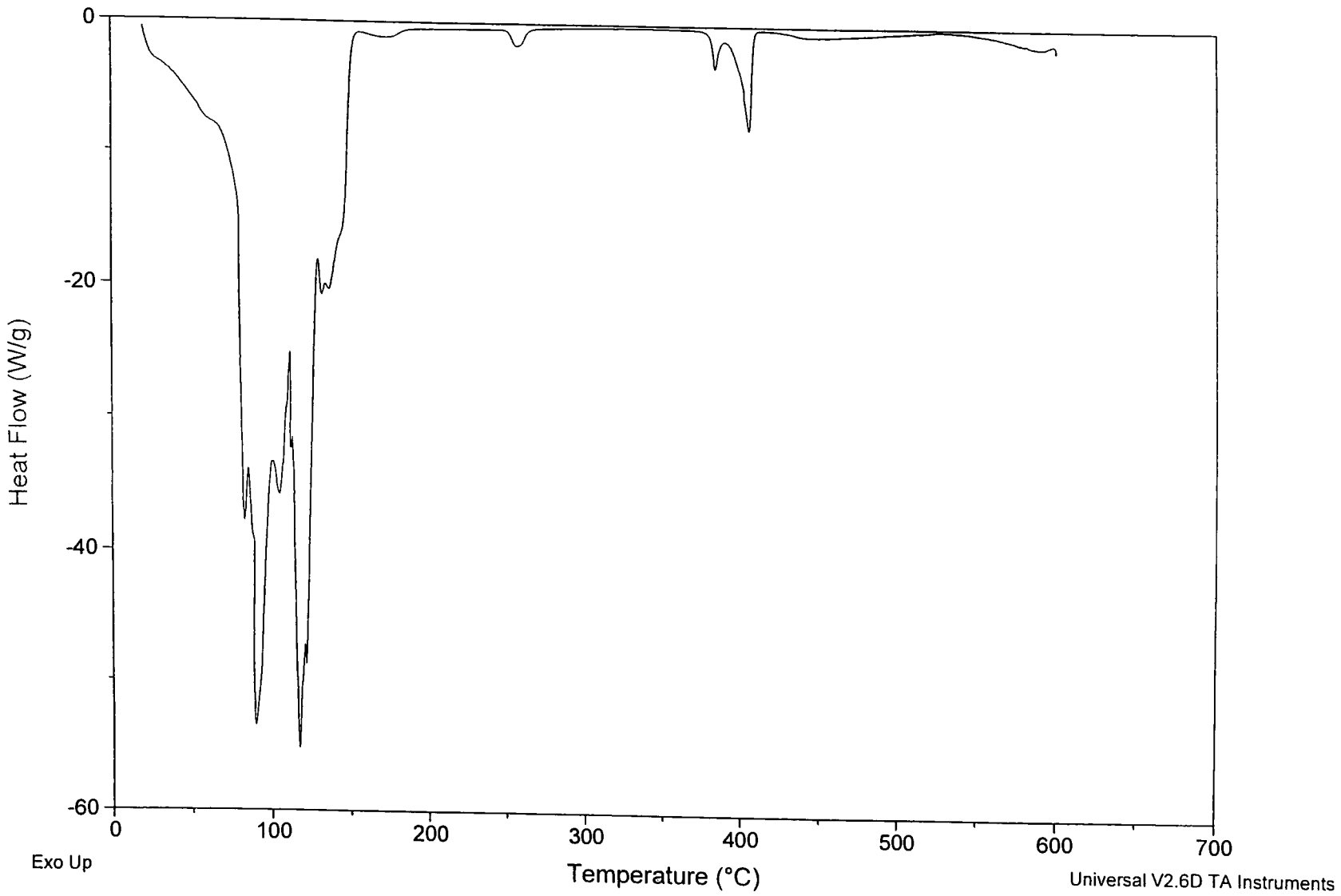


Figure 33. DSC Curve for $Ba(OH)_2*8H_2O$

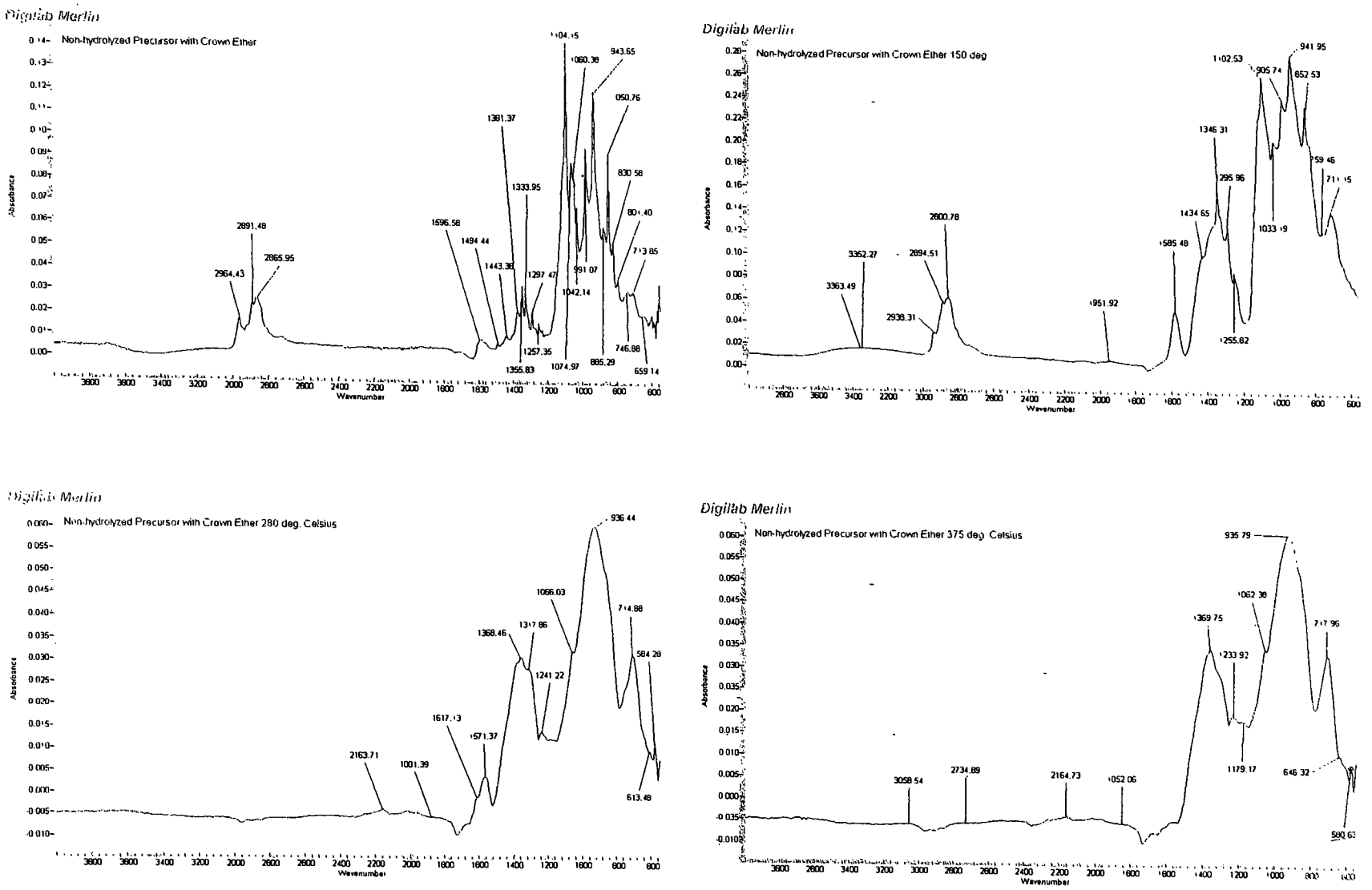


Figure 34. IR Spectra for Non-Hydrolyzed Barium (Crown Ether) Cyclotriboroxane Taken at Various Temperatures

that crown ether is fully removed by 280 °C. Further peak shifts at 375 °C are likely due to rearrangement of atoms.

Figure 35 is a similar set of spectra for the hydrolyzed precursor. The crown ether is removed by 290 °C in this case. Again, the peak shifts at higher temperatures are likely due to structural rearrangement processes.

A few differences between the non-hydrolyzed and hydrolyzed precursor spectra are observed. One major difference is the presence of a peak at 1720 cm^{-1} for the hydrolyzed sample at 150 °C. Another major difference is the presence of peaks at 767.67 and 1587.4 cm^{-1} for the hydrolyzed precursor at 350 °C.

3.3 X-Ray Diffraction of β BBO Powders Prepared From Barium Dimesitylborinate and Barium (Crown Ether) Cyclotriboroxane Precursors

X-Ray Diffraction was performed on precursor powders prepared by both methods. Cu Kα radiation was used at 40 kV and 35 mA. The scans were taken from 10-110° 2θ at 6°/min. The powder diffraction pattern for β–BBO (PDF #38-0722) is shown in Figure 36. If β–BBO is present in any of the samples scanned the peaks should closely match those identified in this PDF file.

3.3.1 X-Ray Diffraction of β–BBO Prepared from Barium Dimesitylborinate Precursor Powders

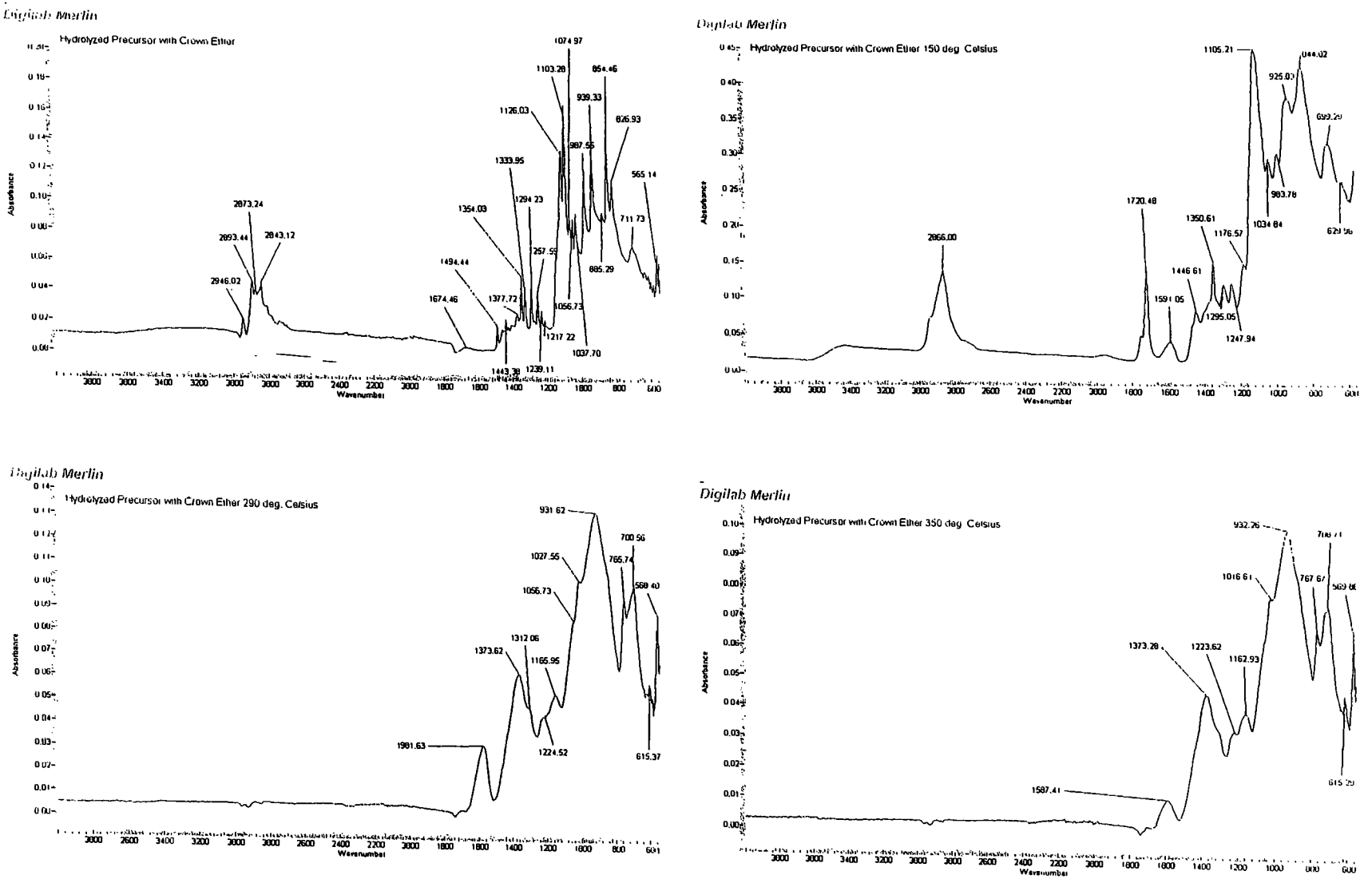


Figure 35. IR Spectra for Hydrolyzed Barium (Crown Ether) Cyclotriboroxane Taken at Various Temperatures

PDF#38-0722 QM=Star d=(Unknown) I=(Unknown)

JADE - PDF Card

Barium Borate

Ba B2 O4

The space group is from Liebertz, J., Stahr, S., Z Kristallogr., 165 91-93 (1983). Rhombohedral cell a=8.387, $GA=96.68

Radiation: CuKa1 Lambda= 1.5406 Filter=

Calibration: d-Cutoff= I/Ic(RIR)=

Ref. Cook, W., Cleveland Crystals, Inc., Cleveland, Ohio, USA. Private Communication (1987)

Rhombohedral (?), R3c(161) Z= mp=

Cell= 12.532x12.726 Pearson: hR0 ($GB)

Dx= Dm= Mwt= 222.95 Vol= 576.95 F(27)=15.5(0.025,71)

Ref: Ibid.

ea= nwB= ey= Sign: 2V=

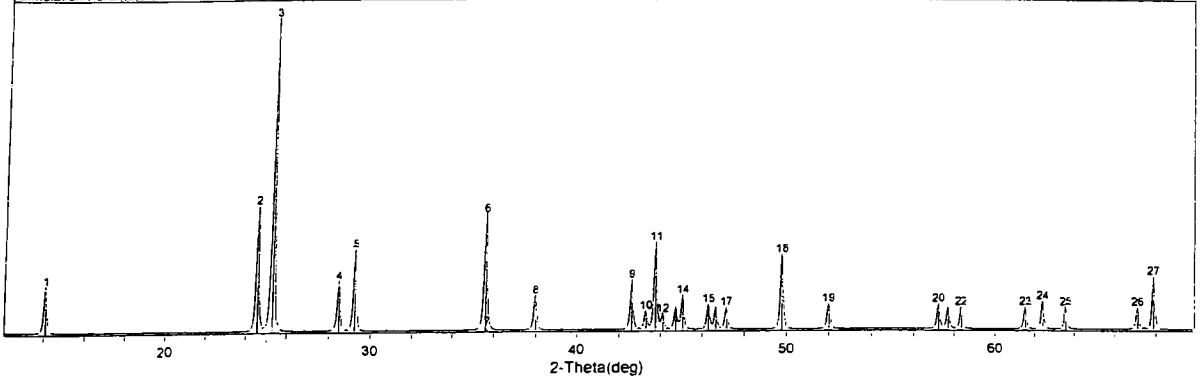
Ref:

27 Reflection(s), Wavelength for Computing Theta = 1.540562<CU>

Strong Line: 3.51/X 3.62/4 2.52/4 2.07/3 3.05/3 1.83/2 2.51/2 1.38/2 3 13/2 2 12/2

#	d(A)	I(f)	h	k	l	2-Theta	#	d(A)	I(f)	h	k	l	2-Theta	#	d(A)	I(f)	h	k	l	2-Theta	#	d(A)	I(f)	h	k	l	2-Theta
1	6.2810	15	1	1	0	14.089																				
2	3.6180	40	3	0	0	24.585																				
3	3.5130	100	1	1	3	25.332																				
4	3.1310	16	2	2	0	28.484																				
5	3.0500	26	1	0	4	29.257																				
6	2.5190	37	2	2	3	35.611																				
7	2.5130	<1	2	1	4	35.699																				
8	2.3660	11	1	4	0	37.999																				
9	2.1200	16	0	0	6	42.611																				
10	2.0880	6	3	3	0	43.297																				
11	2.0670	28	1	4	3	43.759																				
12	2.0510	5	5	0	2	44.118																				
13	2.0240	7	2	4	1	44.738																				
14	2.0100	11	1	1	6	45.067																				
15	1.9590	8	3	2	4	46.308																				
16	1.9450	7	3	1	5	46.661																				
17	1.9250	7	5	1	1	47.175																				
18	1.8300	24	0	3	6	49.785																				
19	1.7570	6	2	2	6	52.005																				
20	1.6080	8	2	5	3	57.244																				
21	1.5960	7	4	2	5	57.715																				
22	1.5800	7	4	1	6	58.355																				
23	1.5060	7	0	7	2	61.524																				
24	1.4870	9	3	3	6	62.398																				
25	1.4620	7	3	4	5	63.588																				
26	1.3937	7	7	0	4	67.103																				
27	1.3794	17	1	1	9	67.893																				
@	End-Of-List <I%-Type = (Unknown)>																									

Simulation Parameters Fixed-Slit Intensities, 2-Theta Range = 12.09 - 69.89, Stepsize = 0.02, FWHM = 0.15, Profile = I/(1+kx^2)^2, k=0.4142/(FWHM/2)^2



R I.T.

Wednesday, Feb 18, 2004 @12:00p

Figure 36. PDF file for β-BBO

Figure 37 shows a typical X-ray diffraction pattern for β–BBO prepared from $Ba[OB(Mes)_2]_2$ single source precursor. This sample was prepared by heat treatment of the precursor at 800 °C. By comparison with the PDF file for β–BBO it is determined that all major peaks closely match those from the experimental diffraction pattern. Table III lists all the identified peaks for the experiment along with the positive matches for β–BBO. These matches indicate that β–BBO has been successfully prepared from the $Ba[OB(Mes)_2]_2$ single source precursor.

3.3.2 X-Ray Diffraction of β–BBO Prepared From Barium (Crown Ether) Cyclotriboroxane Precursor Powders and Powders Prepared Utilizing 2-Ethoxyethanol as Reported by Yogo

Barium (crown ether) cyclotriboroxane precursor powders and powders prepared by Yogo's reported method [11] were heat treated at 550, 650, and 750 °C. The powders heated at various temperatures were monitored by X-ray diffraction to determine if the barium (crown ether) cyclotriboroxane precursor would form β–BBO at lower temperatures than the related powders prepared by Yogo's method. Recall that Yogo's method utilized 2-ethoxyethanol rather than 18-crown-6 (crown ether) as the stabilizer.

Figures 38 through 40 are the diffraction patterns taken at the various temperatures for Yogo's method. At 550 °C it is inconclusive as to whether β–BBO has yet formed. At 650 °C the sample may contain β–BBO, but much of the sample is still amorphous. At 750 °C the diffraction pattern closely matches that for β–BBO. Table IV lists the identified peaks along with the β–BBO matches at this temperature. In the

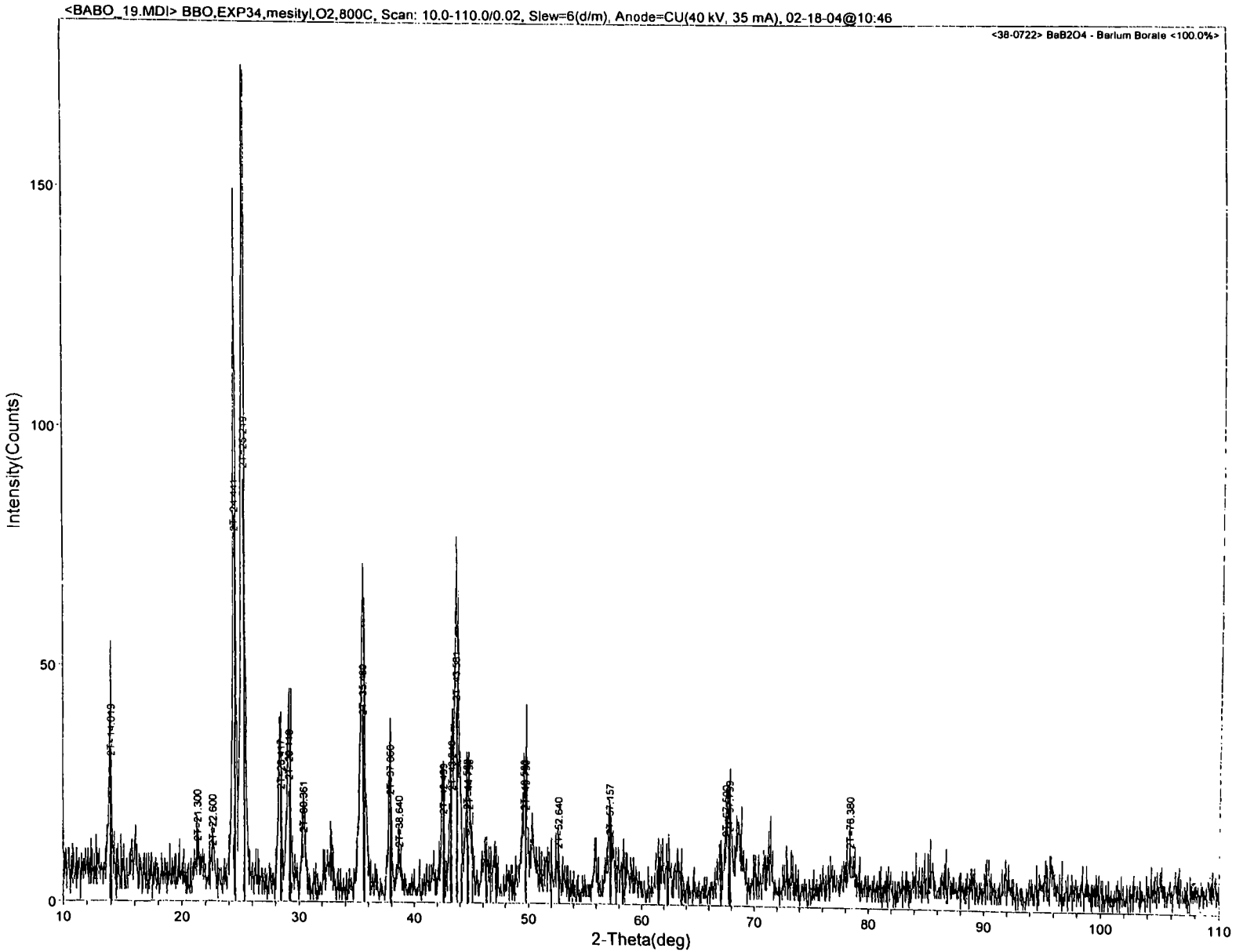


Figure 37. X-Ray Diffraction Pattern After Heating Barium Dimesitylborinate Precursor to 800 °C

Table III. Identified Peaks and Positive Matches to β-BBO for Barium Dimesitylborinate Precursor Heated to 800 °C

<BABO 19.MDI> BBO,EXP34,mesityl,O2,800C [JADE - Peak ID Report]

Scan Parameters: Range = 10.0-110.0/0.02, Slew = 8(d/m), Max-I = 178, Anode = CU(40 kV, 35 mA) Date: 02-18-04@10:48

Search Parameters: Filter = 19(pts), Threshold = 3.0(esd), Peak-Cutoff = 1.0%, 2-Theta Zero Offset = 0.0(deg)

Note: Intensity data from raw counts, Summit peak location, Wavelength for computing d-spacing = 1.540562<CU, K-alpha1>

#	2-Theta	d(A)	BG	Int	I%	Area	A%	FWHM		Phase-ID	d(A)	I%	h	k	l	2-Theta	Delta-2T	#
1	14.019	6.3121	4	51	29.5	10	15.2	0.150	<>	BaB2O4	6.2610	15				14.089	0.070	1
2	21.300	4.1679	3	15	8.7	3	3.8	0.122	<>									2
3	22.800	3.9310	2	14	8.1	3	4.4	0.156	<>									3
4	24.441	3.8390	2	148	85.5	45	70.7	0.239	<>	BaB2O4	3.8160	40				24.585	0.144	4
5	25.219	3.5285	3	173	100.0	63	100.0	0.289	<>	BaB2O4	3.5130	100				25.332	0.113	5
6	28.417	3.1383	5	35	20.2	7	11.0	0.158	<>	BaB2O4	3.1310	18				28.484	0.067	6
7	29.119	3.0641	4	41	23.7	12	19.0	0.231	<>	BaB2O4	3.0490	28				29.267	0.148	7
8	30.381	2.9418	2	20	11.8	6	9.2	0.230	<>									8
9	35.460	2.5294	3	69	39.9	30	47.3	0.343	<>	BaB2O4	2.5190	37				35.611	0.151	9
10	37.660	2.3744	3	38	20.8	8	12.7	0.178	<>	BaB2O4	2.3659	11				38.001	0.141	10
11	38.640	2.3282	2	14	8.1	2	2.8	0.101	<>									11
12	42.499	2.1253	4	26	15.0	6	9.0	0.174	<>	BaB2O4	2.1199	16				42.613	0.114	12
13	43.240	2.0908	5	36	20.8	13	20.5	0.264	<>	BaB2O4	2.0680	6				43.297	0.056	13
14	43.581	2.0750	6	72	41.8	38	59.7	0.415	<>	BaB2O4	2.0689	26				43.761	0.181	14
15	44.582	2.0307	7	25	14.5	5	7.4	0.148	<>									15
16	44.758	2.0232	6	26	15.0	10	14.9	0.288	<>	BaB2O4	2.0239	7				44.741	-0.017	16
17	49.582	1.8370	5	27	15.8	10	15.7	0.292	<>									17
18	49.759	1.8309	3	30	17.3	11	16.9	0.282	<>	BaB2O4	1.8300	24				49.765	0.026	18
19	52.640	1.7373	2	14	8.1	2	2.2	0.080	<>									19
20	57.157	1.6102	3	19	11.0	8	12.5	0.328	<>	BaB2O4	1.6080	8				57.244	0.087	20
21	87.500	1.3885	5	18	10.4	4	5.4	0.149	<>									21
22	87.799	1.3811	7	18	10.4	5	7.9	0.220	<>	BaB2O4	1.3794	17				87.893	0.094	22
23	78.380	1.2190	3	15	8.7	2	2.5	0.082	<>									23
@	End-of-List															Average Delta 2-Theta = 0.101		
	> PDF#38-0722 ---------- BaB2O4 - Barium Borate																	

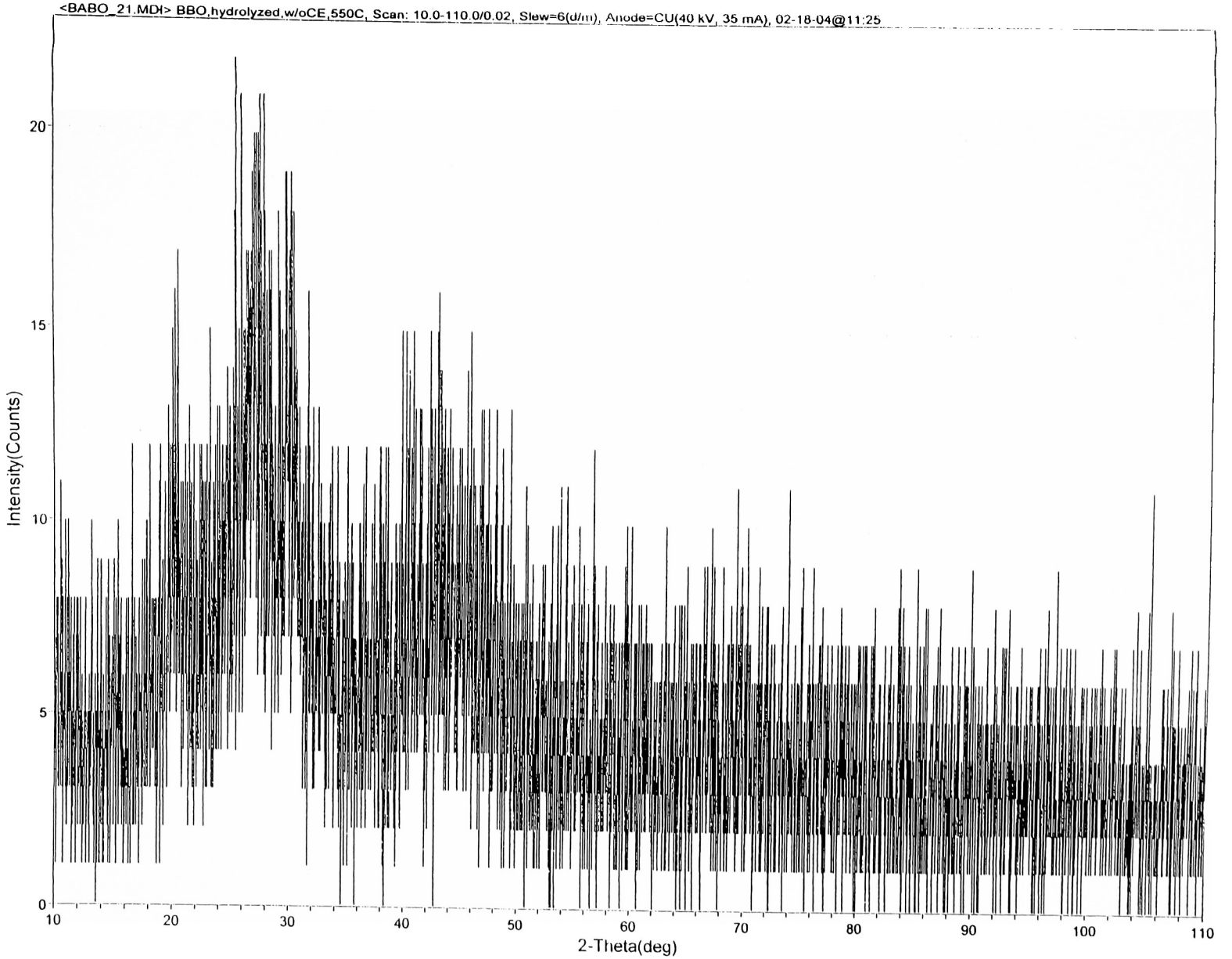


Figure 38. X-Ray Diffraction Pattern After Heating Yogo's Precursor to 550 °C

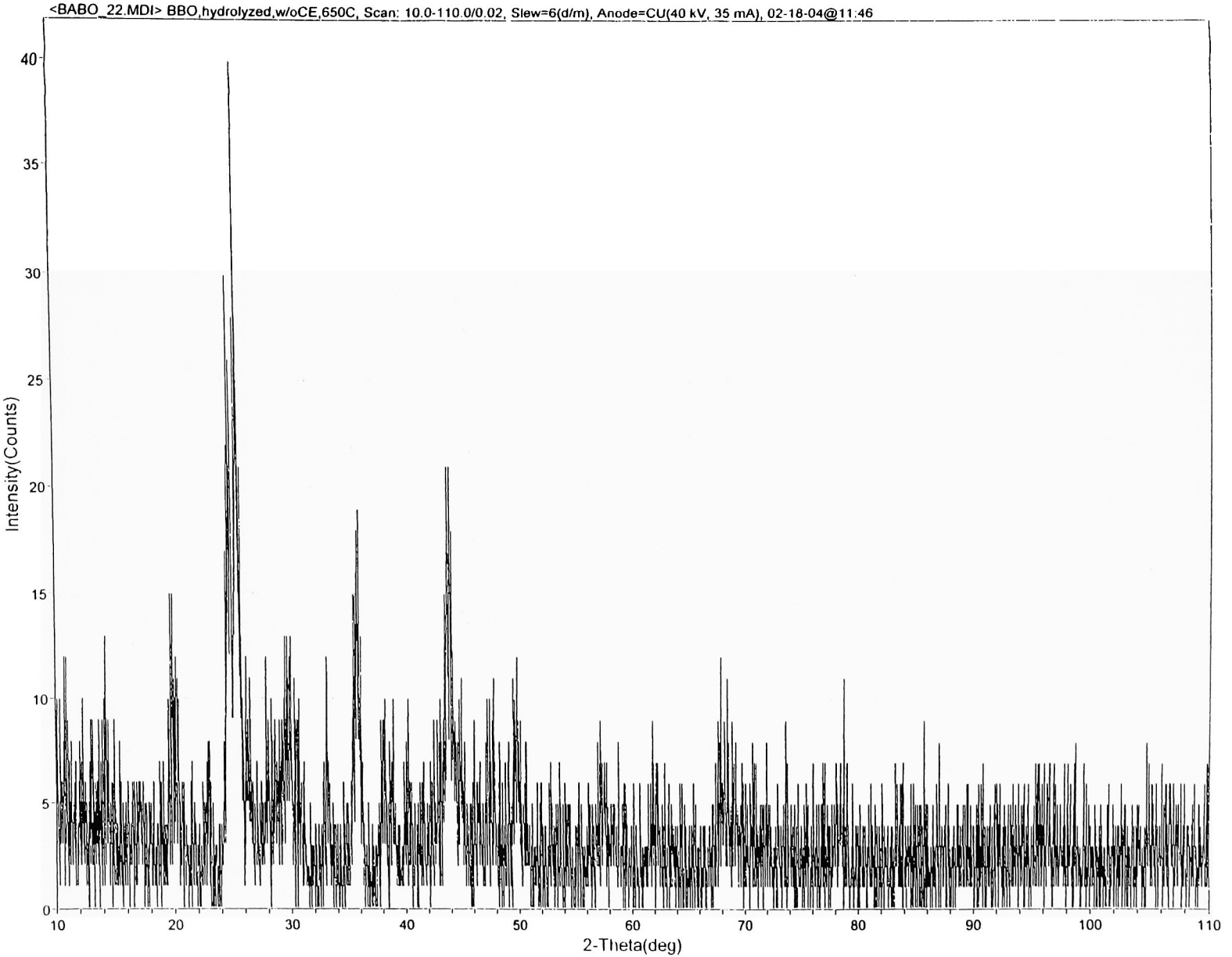


Figure 39. X-Ray Diffraction Pattern After Heating Yogo's Precursor to 650 °C

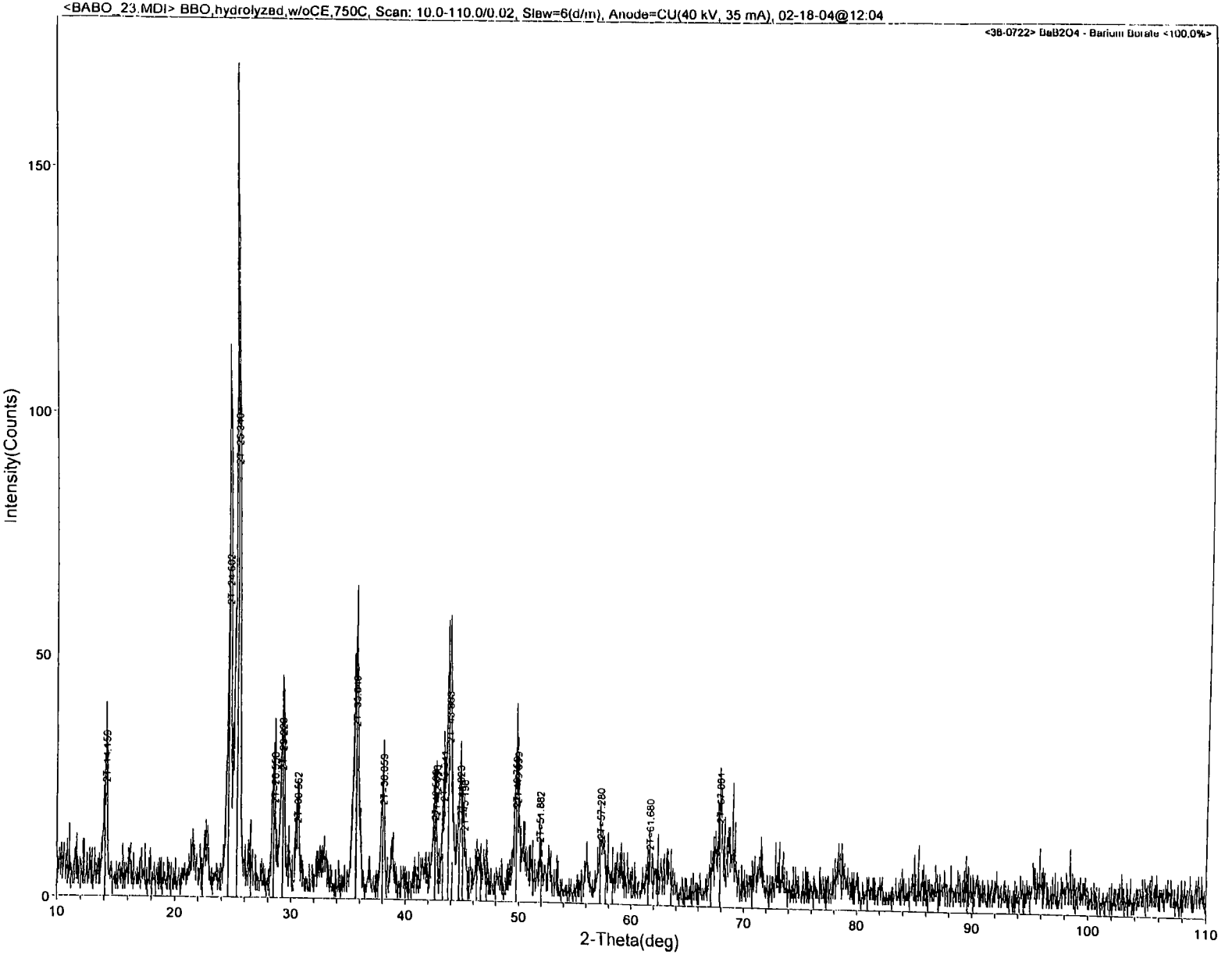


Figure 40. X-Ray Diffraction Pattern After Heating Yogo's Precursor to 750 °C

Table IV. Identified Peaks and Positive Matches to β-BBO for Yogo's Precursor Heated to 750 °C

<BABO_23.MDI> BBO,hydrolyzed,w/oCE,750C [JADE - Peak ID Report]

Scan Parameters: Range = 10.0-110.0/0.02, Slew = 6(d/m), Max-I = 172, Anode = CU(40 kV, 35 mA) Date: 02-16-04@12:04

Search Parameters: Filter = 19(pts), Threshold = 3.0(esd), Peak-Cutoff = 1.0%, 2-Theta Zero Offset = 0.0(deg)

Note: Intensity data from raw counts, Summit peak location, Wavelength for computing d-spacing = 1.540562<CU, K-alpha1>

#	2-Theta	d(A)	BG	Int	I%	Area	A%	FWHM		Phase-ID	d(A)	I%	h	k	l	2-Theta	Delta-2T	#
1	14.159	6.2496	2	36	22.6	6	13.5	0.166	<>	BaB2O4	6.2610	15				14.069	-0.071	1
2	24.602	3.6156	3	111	66.1	36	59.6	0.254	<>	BaB2O4	3.6160	40				24.565	-0.017	2
3	25.340	3.5119	4	166	100.0	60	100.0	0.262	<>	BaB2O4	3.5130	100				25.332	-0.006	3
4	26.556	3.1230	6	27	16.1	5	7.2	0.126	<>	BaB2O4	3.1310	16				26.464	-0.074	4
5	29.223	3.0535	4	42	25.0	15	23.9	0.269	<>	BaB2O4	3.0490	26				29.267	0.044	5
6	30.562	2.9227	2	22	13.1	6	9.6	0.210	<>									6
7	35.640	2.5170	2	63	37.5	27	44.6	0.337	<>	BaB2O4	2.5190	37				35.611	-0.029	7
8	36.059	2.3624	2	31	16.5	7	11.5	0.175	<>	BaB2O4	2.3659	11				36.001	-0.056	8
9	42.560	2.1215	4	23	13.7	7	10.6	0.216	<>	BaB2O4	2.1199	16				42.613	0.033	9
10	42.696	2.1159	4	25	14.9	4	5.5	0.104	<>									10
11	43.341	2.0660	5	30	17.9	7	10.5	0.166	<>	BaB2O4	2.0660	6				43.297	-0.044	11
12	43.663	2.0624	7	52	31.0	23	37.6	0.343	<>	BaB2O4	2.0669	26				43.761	-0.101	12
13	44.623	2.0204	6	21	12.5	6	9.0	0.202	<>	BaB2O4	2.0239	7				44.741	-0.062	13
14	45.196	2.0045	5	17	10.1	2	3.3	0.092	<>	BaB2O4	2.0099	11				45.069	-0.126	14
15	49.759	1.6309	4	26	16.7	12	16.6	0.317	<>	BaB2O4	1.6300	24				49.765	0.026	15
16	49.699	1.6261	4	30	17.9	10	15.7	0.247	<>									16
17	51.662	1.7606	3	15	6.9	2	1.7	0.054	<>	BaB2O4	1.7569	6				52.006	0.125	17
18	57.260	1.6071	3	16	10.7	6	6.7	0.229	<>	BaB2O4	1.6060	6				57.244	-0.036	18
19	61.660	1.5026	2	14	6.3	2	2.0	0.069	<>	BaB2O4	1.5060	7				61.524	-0.156	19
20	67.661	1.3796	6	23	13.7	6	6.5	0.175	<>	BaB2O4	1.3794	17				67.693	0.011	20
@	End-of-List																	
	> PDF#36-0722 ——— BaB2O4 - Barium Borate															Average Delta 2-Theta = 0.061		

literature describing this method the transition to the β–BBO phase was reported to have occurred at 650 °C [11]. The results obtained in this experiment found that the bulk of the sample undergoes this transition at a temperature closer to 750 °C.

Figures 41 through 43 are the diffraction patterns taken at the various temperatures for non-hydrolyzed barium (crown ether) cyclotriboroxane powders. At 550 °C the diffraction pattern already matches that of β–BBO. The patterns at 650 and 750 °C also reveal the presence of β–BBO. Table V lists the identified peaks and the matches to β–BBO for the sample treated at 550 °C. This comparison shows that the transition to the β–BBO phase has already occurred by this temperature. The identified peaks for the samples heated to 650 and 750 °C are shown in Tables VI and VII. The sample heated at 650 °C shows a low signal to noise ratio. This could be caused by a non-uniform coverage of powder on the sample holder within the X-ray diffractometer.

Figures 44 through 46 show the diffraction patterns taken at various temperatures for hydrolyzed barium (crown ether) cyclotriboroxane powders. At 550 °C the diffraction pattern reveals β–BBO. This phase is also found to be present at 650 and 750 °C. The highest signal to noise ratio is found in the sample at 750 °C. It seems that the complete transition of the bulk to β–BBO may require higher temperatures in the hydrolyzed form. The identified peaks and matches to β–BBO for these samples can be seen in Tables VIII, IX, and X.

From this experimentation it has been determined that β–BBO is formed by the solid state thermolysis of both barium dimesitylborinate and barium (crown ether) cyclotriboroxane precursors. It has also been determined that β–BBO forms at 550 °C for barium (crown ether) cyclotriboroxane precursors. The precursor developed by Yogo

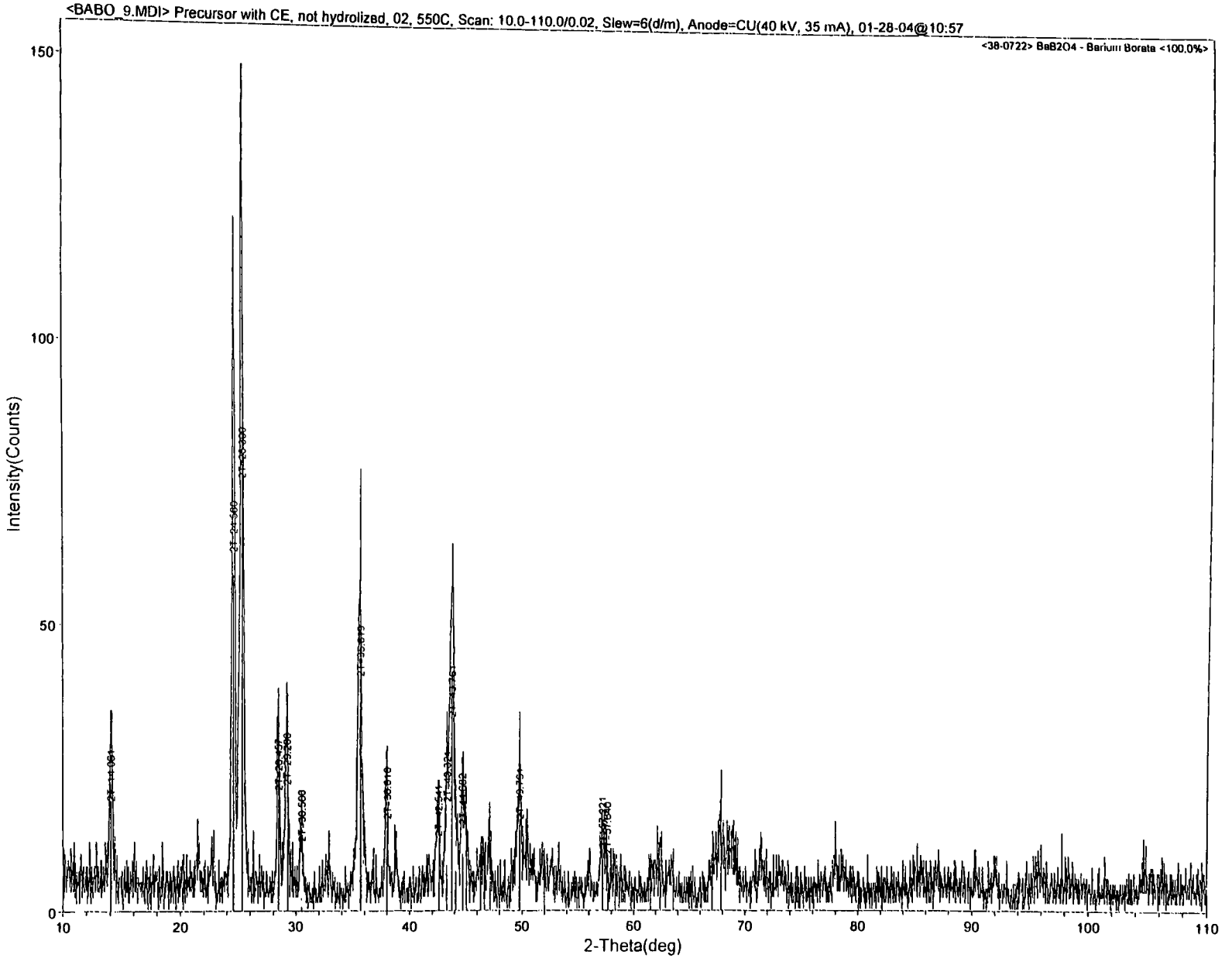


Figure 41. X-Ray Diffraction Pattern After Heating Non-Hydrolyzed Barium (Crown Ether) Cyclotriboroxane to 550 °C

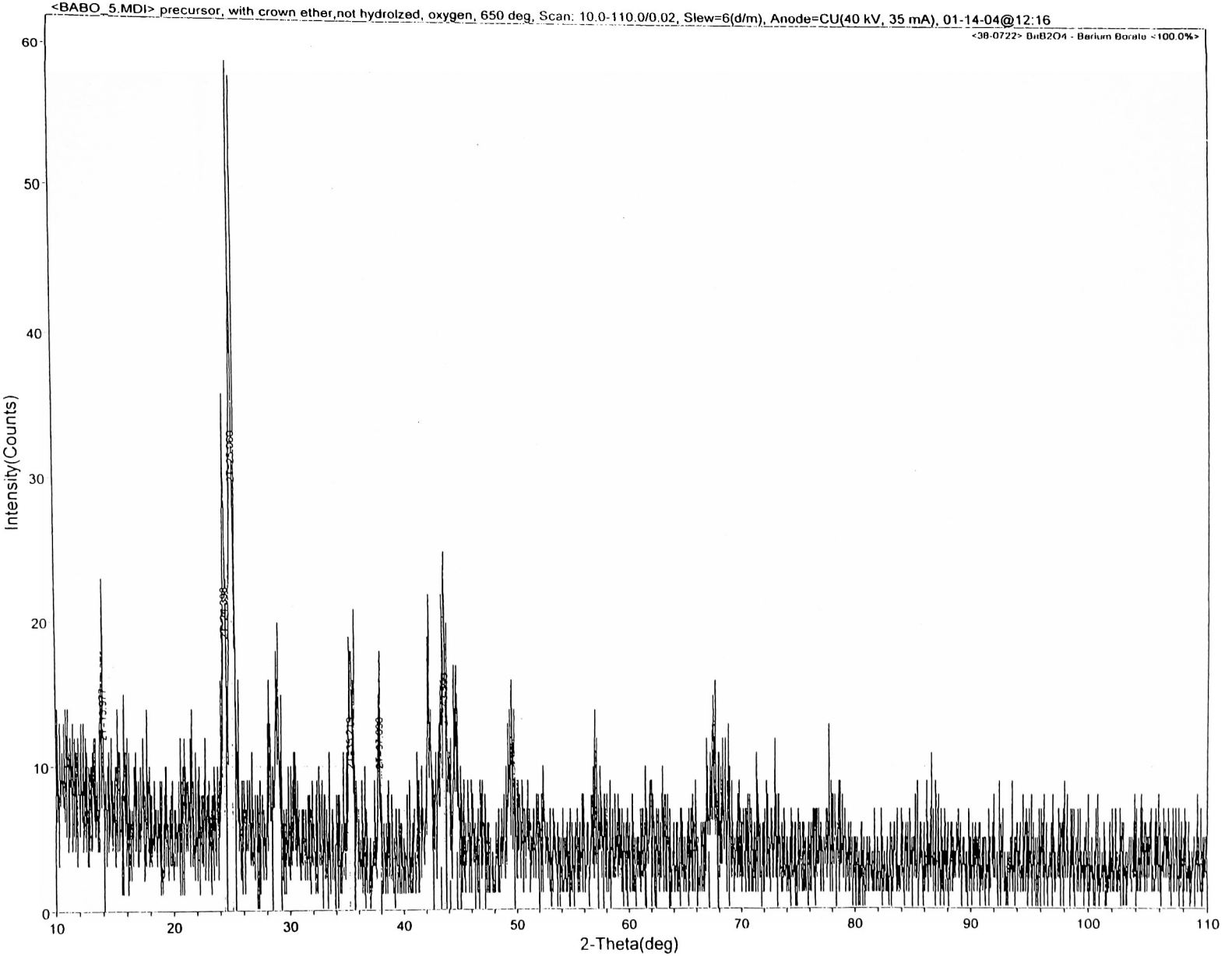


Figure 42. X-Ray Diffraction Pattern After Heating Non-Hydrolyzed Barium (Crown Ether) Cyclotriboroxane to 650 °C

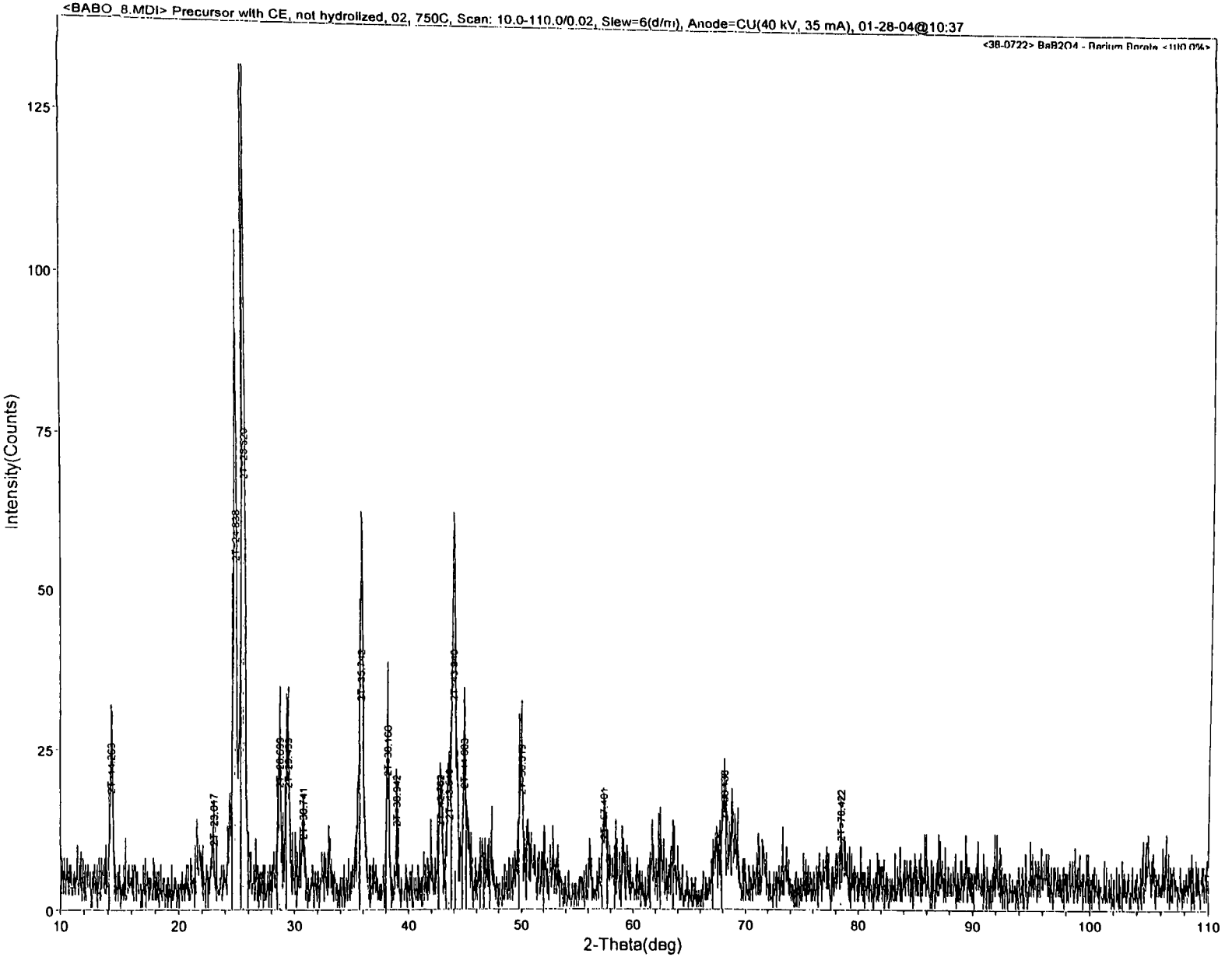


Figure 43. X-Ray Diffraction Pattern After Heating Non-Hydrolyzed Barium (Crown Ether) Cyclotriboroxane to 750 °C

Table V. Identified Peaks and Positive Matches to β-BBO for Non-Hydrolyzed Barium (Crown Ether) Cyclotriboroxane Heated to 550 °C

<BABO_9.MDI> Precursor with CE, not hydrolized, 02, 550C [JADE - Peak ID Report]

Scan Parameters: Range = 10.0-110.0/0.02, Slew = 8(d/m), Max-I = 149, Anode = CU(40 kV, 35 mA) Date: 01-28-04@10:57

Search Parameters: Filter = 19(pts), Threshold = 3.0(esd), Peak-Cutoff = 1.0%, 2-Theta Zero Offset = 0.0(deg)

Note: Intensity data from raw counts, Summit peak location, Wavelength for computing d-spacing = 1.540582<CU, K-alpha1>

#	2-Theta	d(A)	BG	Int	I%	Area	A%	FWHM		Phase-ID	d(A)	I%	h	k	l	2-Theta	Delta-2T	#
1	14.061	8.2931	3	32	23.2	9	20.6	0.220	<>	BaB2O4	8.2810	15				14.089	0.027	1
2	24.580	3.8218	13	109	79.0	27	82.1	0.195	<>	BaB2O4	3.8180	40				24.585	0.025	2
3	25.300	3.5174	11	138	100.0	43	100.0	0.248	<>	BaB2O4	3.5130	100				25.332	0.032	3
4	28.457	3.1340	4	35	25.4	8	17.4	0.170	<>	BaB2O4	3.1310	18				28.484	0.027	4
5	29.200	3.0558	4	38	28.1	9	19.8	0.188	<>	BaB2O4	3.0490	28				29.287	0.087	5
6	30.500	2.9285	2	19	13.8	5	9.5	0.172	<>									6
7	35.819	2.5185	2	78	55.1	28	83.4	0.285	<>	BaB2O4	2.5190	37				35.811	-0.007	7
8	38.018	2.3849	3	28	18.8	5	11.2	0.147	<>	BaB2O4	2.3859	11				38.001	-0.017	8
9	42.541	2.1233	5	18	13.0	4	7.3	0.140	<>	BaB2O4	2.1199	18				42.813	0.072	9
10	43.321	2.0889	8	29	21.0	7	15.4	0.182	<>	BaB2O4	2.0880	8				43.297	-0.025	10
11	43.781	2.0889	7	58	42.0	27	82.5	0.389	<>	BaB2O4	2.0889	28				43.781	0.001	11
12	44.882	2.0284	8	21	15.2	4	9.3	0.151	<>	BaB2O4	2.0239	7				44.741	0.059	12
13	49.781	1.8308	3	25	18.1	8	18.7	0.258	<>	BaB2O4	1.8300	24				49.785	0.025	13
14	57.221	1.8088	2	18	11.8	8	13.4	0.287	<>	BaB2O4	1.8080	8				57.244	0.023	14
15	57.840	1.5979	2	14	10.1	2	3.9	0.095	<>	BaB2O4	1.5959	7				57.719	0.078	15
@	End-of-List																	

Average Delta 2-Theta = 0.035

> PDF#38-0722 ---------- BaB2O4 - Barium Borate

Table VI. Identified Peaks and Positive Matches to β-BBO for Non-Hydrolyzed Barium (Crown Ether) Cyclotriboroxane Heated to 650 °C

<BABO_5.MDI> precursor, with crown ether,not hydrolzed, oxygen, 650 deg [JADE - Peak ID Report]

Scan Parameters: Range = 10.0-110.0/0.02, Slew = 6(d/m), Max-I = 59, Anode = CU(40 kV, 35 mA) Date: 01-14-04@12:16

Search Parameters: Filter = 19(pts), Threshold = 3.0(esd), Peak-Cutoff = 1.0%, 2-Theta Zero Offset = 0.0(deg)

Note: Intensity data from raw counts, Summit peak location, Wavelength for computing d-spacing = 1.540562<CU, K-alpha1>

#	2-Theta	d(A)	BG	Int	I%	Area	A%	FWHM		Phase-ID	d(A)	I%	h	k	l	2-Theta	Delta-2T	#
1	13.977	6.3310	6	17	32.1	2	6.9	0.064	<>	BaB2O4	6.2610	15				14.069	0.112	1
2	24.398	3.6453	9	27	50.9	5	30.4	0.137	<>	BaB2O4	3.6160	40				24.565	0.167	2
3	25.060	3.5504	6	53	100.0	16	100.0	0.229	<>	BaB2O4	3.5130	100				25.332	0.271	3
4	35.219	2.5461	3	15	28.3	5	27.4	0.222	<>									4
5	37.636	2.3757	2	16	30.2	3	16.0	0.137	<>	BaB2O4	2.3659	11				36.001	0.163	5
6	43.599	2.0742	4	21	39.6	6	46.9	0.263	<>	BaB2O4	2.0669	26				43.761	0.163	6
@	End-of-List															Average Delta 2-Theta = 0.179		
	> PDF#36-0722 ---------- BaB2O4 - Barium Borate																	

Table VII. Identified Peaks and Positive Matches to β-BBO for Non-Hydrolyzed Barium (Crown Ether) Cyclotriboroxane Heated to 750 °C

<BABO_6.MDI> Precursor with CE, not hydrolized, 02, 750C [JADE - Peak ID Report]

Scan Parameters: Range = 10.0-110.0/0.02, Slew = 6(d/m), Max-I = 133, Anode = CU(40 kV, 35 mA) Date: 01-26-04@10:37

Search Parameters: Filter = 19(pts), Threshold = 3.0(esd), Peak-Cutoff = 1.0%, 2-Theta Zero Offset = 0.0(deg)

Note: Intensity data from raw counts, Summit peak location, Wavelength for computing d-spacing = 1.540562<CU, K-alpha1>

#	2-Theta	d(A)	BG	Int	I%	Area	A%	FWHM		Phase-ID	d(A)	I%	h	k	l	2-Theta	Delta-2T	#
1	14.263	6.2046	2	30	23.1	6	16.3	0.196	<>	BaB2O4	6.2610	15				14.069	-0.174	1
2	23.017	3.8609	2	15	11.5	2	3.0	0.073	<>									2
3	24.636	3.5617	4	103	79.2	37	79.6	0.260	<>	BaB2O4	3.6160	40				24.565	-0.253	3
4	25.520	3.4675	3	130	100.0	46	100.0	0.279	<>	BaB2O4	3.5130	100				25.332	-0.166	4
5	26.699	3.1060	5	30	23.1	6	11.4	0.136	<>	BaB2O4	3.1310	16				26.464	-0.216	5
6	29.439	3.0315	5	30	23.1	6	16.4	0.196	<>	BaB2O4	3.0490	26				29.267	-0.172	6
7	30.741	2.9061	2	16	12.3	3	5.6	0.131	<>									7
8	35.742	2.5101	2	61	46.9	24	52.1	0.309	<>	BaB2O4	2.5130	20				35.699	-0.043	8
9	36.160	2.3584	2	37	26.5	7	15.0	0.147	<>	BaB2O4	2.3659	11				36.001	-0.159	9
10	36.942	2.3109	3	19	14.6	2	2.9	0.056	<>									10
11	42.762	2.1129	3	20	15.4	6	11.3	0.204	<>	BaB2O4	2.1199	16				42.613	-0.149	11
12	43.540	2.0769	6	19	14.6	7	14.7	0.260	<>	BaB2O4	2.0669	26				43.761	0.221	12
13	43.940	2.0589	7	56	43.1	24	52.4	0.339	<>	BaB2O4	2.0510	5				44.116	0.176	13
14	44.663	2.0276	7	28	21.5	4	6.6	0.067	<>	BaB2O4	2.0239	7				44.741	-0.142	14
15	50.019	1.8220	6	27	20.6	5	10.6	0.145	<>	BaB2O4	1.8300	24				49.765	-0.234	15
16	57.401	1.6040	3	16	12.3	4	7.9	0.176	<>	BaB2O4	1.6060	8				57.244	-0.157	16
17	66.136	1.3750	7	17	13.1	2	4.0	0.066	<>	BaB2O4	1.3794	17				67.693	-0.245	17
18	76.422	1.2165	3	15	11.5	2	2.7	0.065	<>									18
@	End-of-List															Average Delta 2-Theta = 0.161		
	> PDF#36-0722 ---------- BaB2O4 - Barium Borate																	

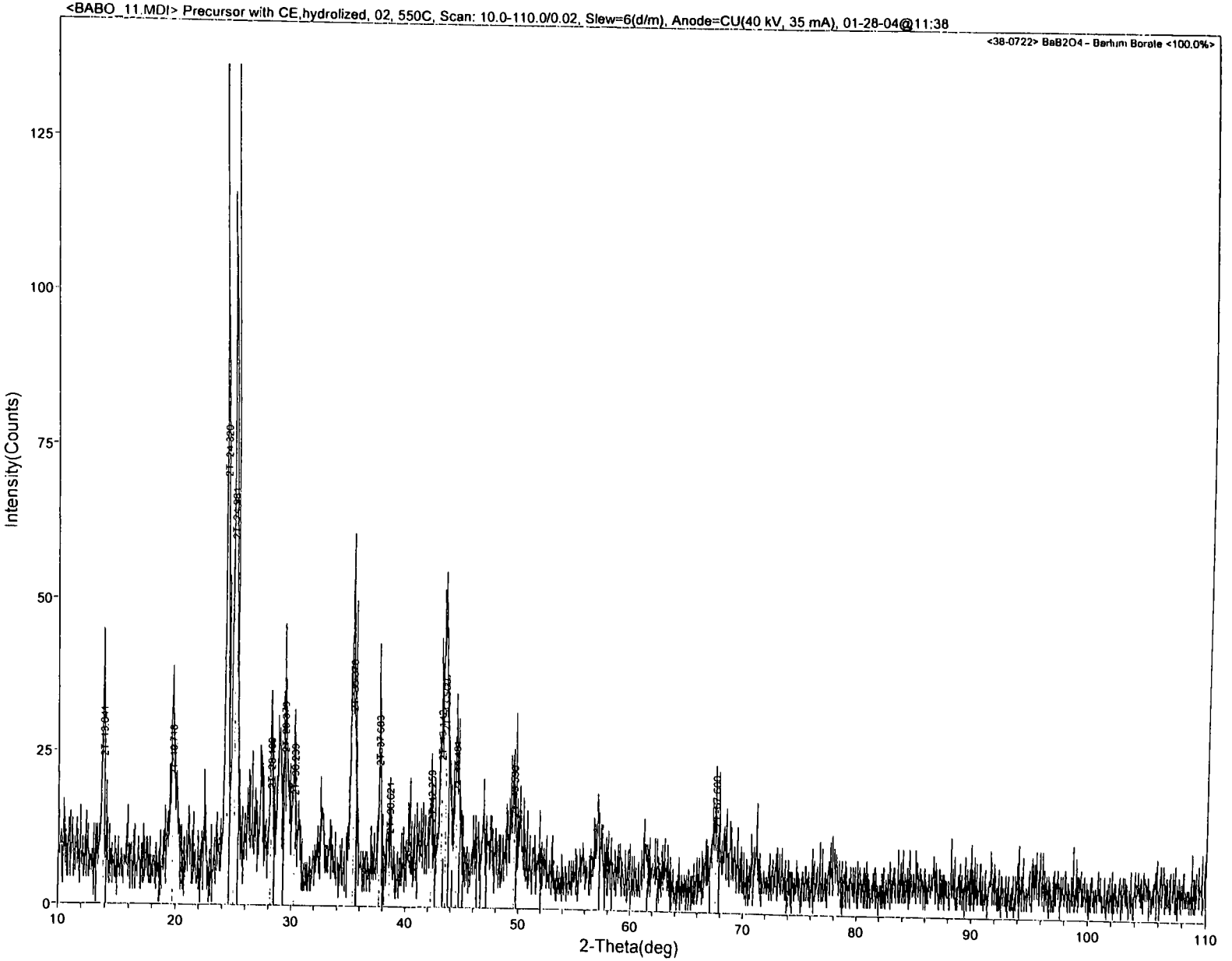


Figure 44. X-Ray Diffraction Pattern After Heating Hydrolyzed Barium (Crown Ether) Cyclotriboroxane to 550 °C

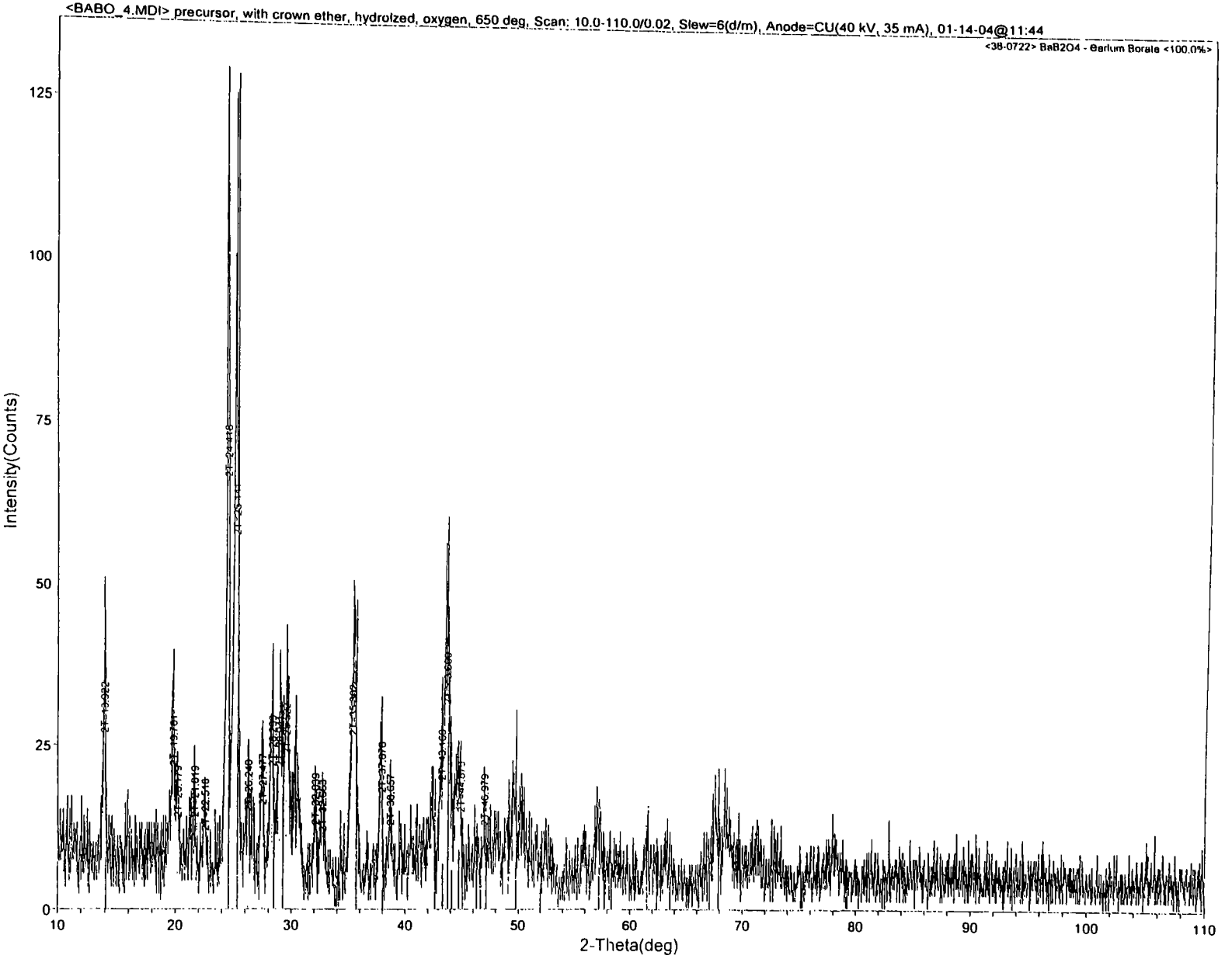


Figure 45. X-Ray Diffraction Pattern After Heating Hydrolyzed Barium (Crown Ether) Cyclotriboroxane to 650 °C

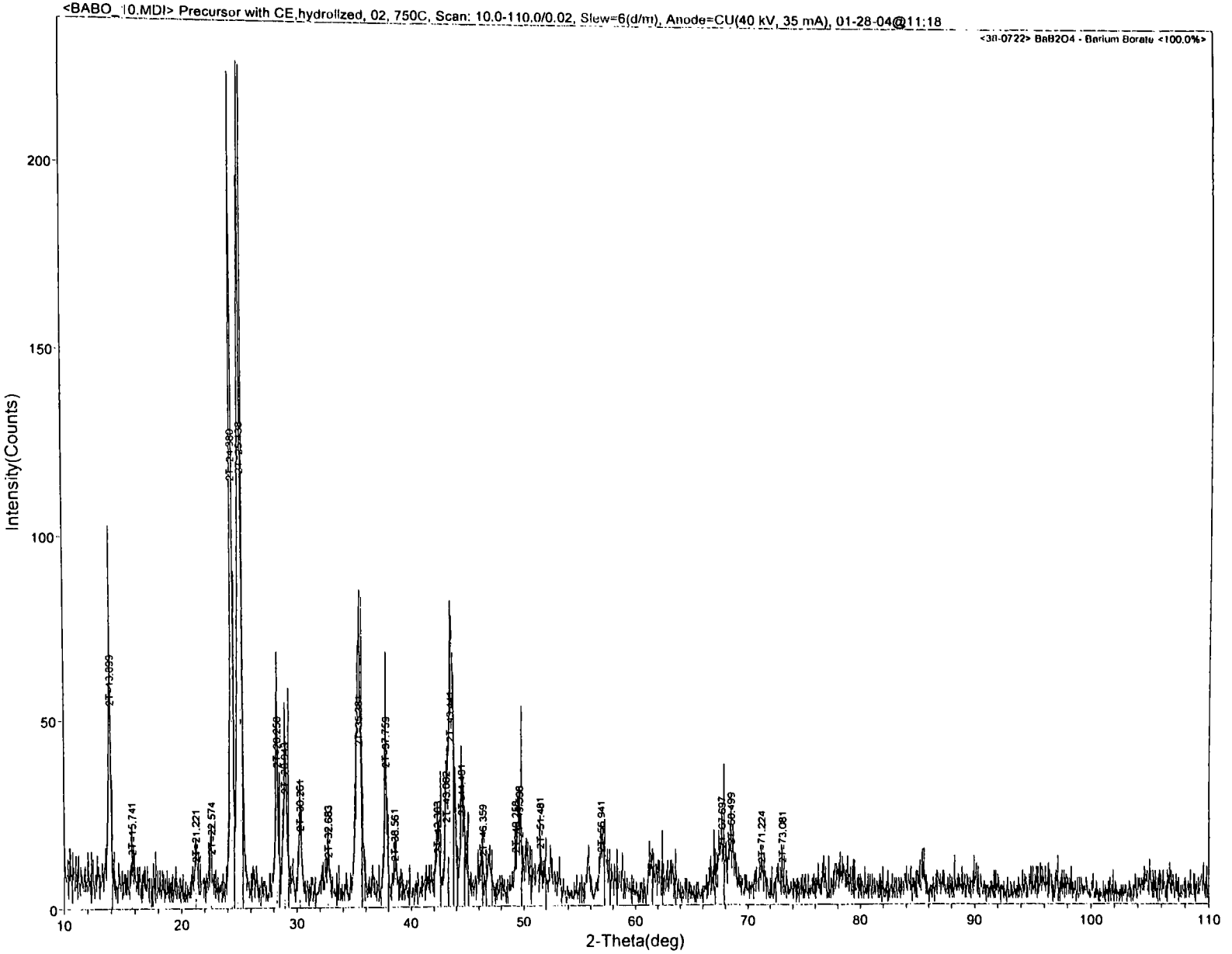


Figure 46. X-Ray Diffraction Pattern After Heating Hydrolyzed Barium (Crown Ether) Cyclotriboroxane to 750 °C

Table VIII. Identified Peaks and Positive Matches to β-BBO for Hydrolyzed Barium (Crown Ether) Cyclotriboroxane Heated to 550 °C

<BABO_11.MDI> Precursor with CE,hydrolized, 02, 550C

[JADE - Peak ID Report]

Scan Parameters: Range = 10.0-110.0/0.02, Slew = 6(d/m), Max-I = 137, Anode = CU(40 kV, 35 mA)

Date: 01-28-04@11:38

Search Parameters: Filter = 19(pts), Threshold = 3.0(esd), Peak-Cutoff = 1.0%, 2-Theta Zero Offset = 0.0(deg)

Note: Intensity data from raw counts, Summit peak location, Wavelength for computing d-spacing = 1.540562<CU, K-alpha1>

#	2-Theta	d(A)	BG	Int	I%	Area	A%	FWHM		Phase-ID	d(A)	I%	h	k	l	2-Theta	Delta-2T	#
1	13.841	6.3930	5	40	33.1	7	22.0	0.120	<>	BaB2O4	6.2810	15				14.089	0.248	1
2	19.718	4.4986	5	34	28.1	16	57.0	0.367	<>									2
3	24.320	3.6569	16	121	100.0	21	75.0	0.136	<>	BaB2O4	3.6180	40				24.585	0.265	3
4	24.981	3.5615	16	100	82.6	28	100.0	0.219	<>									4
5	28.199	3.1620	9	26	21.5	6	18.5	0.156	<>	BaB2O4	3.1310	16				28.484	0.285	5
6	29.379	3.0377	12	34	28.1	4	12.4	0.080	<>	BaB2O4	3.0490	26				29.267	-0.112	6
7	30.239	2.9532	11	21	17.4	3	8.8	0.092	<>									7
8	35.378	2.5350	4	57	47.1	22	80.1	0.308	<>	BaB2O4	2.5190	37				35.611	0.233	8
9	37.683	2.3851	4	39	32.2	7	24.4	0.137	<>									9
10	38.621	2.3293	3	18	14.9	4	12.1	0.147	<>									10
11	42.259	2.1368	8	17	14.0	2	5.2	0.067	<>									11
12	43.142	2.0951	9	35	28.9	11	37.9	0.237	<>	BaB2O4	2.0880	6				43.297	0.155	12
13	43.500	2.0787	10	45	37.2	22	78.2	0.380	<>									13
14	44.481	2.0351	10	25	20.7	4	13.5	0.118	<>	BaB2O4	2.0239	7				44.741	0.260	14
15	49.596	1.8365	8	18	14.9	3	7.7	0.094	<>	BaB2O4	1.8300	24				49.785	0.189	15
16	67.600	1.3847	7	17	14.0	2	5.9	0.076	<>	BaB2O4	1.3794	17				67.893	0.293	16

@ End-of-List

Average Delta 2-Theta = 0.227

> PDF#38-0722 ---------- BaB2O4 - Barium Borate

Table IX. Identified Peaks and Positive Matches to β-BBO for Hydrolyzed Barium (Crown Ether) Cyclotriboroxane Heated to 650 °C

<BABO_4.MDI> precursor, with crown ether, hydrolzed, oxygen, 650 deg [JADE - Peak ID Report]

Scan Parameters: Range = 10.0-110.0/0.02, Slew = 6(d/m), Max-I = 130, Anode = CU(40 kV, 35 mA) Date: 01-14-04@11:44

Search Parameters: Filter = 19(pts), Threshold = 3.0(esd), Peak-Cutoff = 1.0%, 2-Theta Zero Offset = 0.0(deg)

Note: Intensity data from raw counts, Summit peak location, Wavelength for computing d-spacing = 1.540562<CU, K-alpha1>

#	2-Theta	d(A)	BG	Int	I%	Area	A%	FWHM		Phase-ID	d(A)	I%	h	k	l	2-Theta	Delta-2T	#
1	13.922	6.3556	5	46	37.1	9	23.1	0.152	<>	BaB2O4	6.2610	15				14.069	0.167	1
2	19.761	4.4646	6	34	27.4	8	20.3	0.160	<>									2
3	20.179	4.3969	6	16	14.5	3	6.4	0.106	<>									3
4	21.619	4.1072	5	20	16.1	3	5.9	0.090	<>									4
5	22.516	3.9452	3	17	13.7	4	6.7	0.155	<>									5
6	24.416	3.6423	6	124	100.0	30	78.5	0.191	<>	BaB2O4	3.6160	40				24.565	0 167	6
7	25.141	3.5393	7	105	84.7	36	100.0	0.266	<>	BaB2O4	3.5130	100				25.332	0 191	7
6	26.240	3.3935	6	20	16.1	3	6.5	0.096	<>									6
9	27.477	3.2434	6	23	16.5	4	10.5	0.136	<>									9
10	26.299	3.1510	11	30	24.2	5	11.6	0.117	<>	BaB2O4	3.1310	16				26.464	0.165	10
11	26.941	3.0625	11	29	23.4	5	13.1	0.136	<>									11
12	29.522	3.0233	12	32	25.6	9	22.4	0.211	<>	BaB2O4	3.0490	26				29.267	-0.255	12
13	32.039	2.7912	5	17	13.7	3	6.4	0.114	<>									13
14	32.663	2.7393	4	17	13.7	5	10.6	0.189	<>									14
15	35.302	2.5404	3	46	36.7	21	53.4	0.337	<>									15
16	37.676	2.3733	4	29	23.4	5	10.7	0.112	<>	BaB2O4	2.3659	11				36.001	0.123	16
17	36.657	2.3272	3	20	16.1	4	9.6	0.149	<>									17
16	43.160	2.0943	6	26	22.6	9	22.1	0.239	<>	BaB2O4	2.0660	6				43.297	0.137	18
19	43.600	2.0742	10	51	41.1	20	50.4	0.299	<>	BaB2O4	2.0669	26				43.761	0.161	19
20	44.676	2.0161	7	19	15.3	3	5.7	0.091	<>	BaB2O4	2.0239	7				44.741	-0.135	20
21	46.979	1.9326	5	17	13.7	2	3.2	0.056	<>	BaB2O4	1.9249	7				47.177	0.196	21

@ End-of-List

Average Delta 2-Theta = 0.172

> PDF#36-0722 ---------- BaB2O4 - Barium Borate

Table X. Identified Peaks and Positive Matches to β-BBO for Hydrolyzed Barium (Crown Ether) Cyclotriboroxane Heated to 750 °C

<BABO_10.MDI> Precursor with CE,hydrolized, 02, 750C [JADE - Peak ID Report]

Scan Parameters: Range = 10.0-110.0/0.02, Slew = 6(d/m), Max-I = 226, Anode = CU(40 kV, 35 mA) Date: 01-28-04@11:18

Search Parameters: Filter = 19(pts), Threshold = 3.0(esd), Peak-Cutoff = 1.0%, 2-Theta Zero Offset = 0.0(deg)

Note: Intensity data from raw counts, Summit peak location, Wavelength for computing d-spacing = 1.540562<CU, K-alpha1>

#	2-Theta	d(A)	BG	Int	I%	Area	A%	FWHM		Phase-ID	d(A)	I%	h	k	l	2-Theta	Delta-2T	#
1	13.699	6.3661	3	100	44.6	19	25.6	0.147	<>	BaB2O4	6.2610	15				14.069	0.189	1
2	15.741	5.6251	4	16	6.0	2	2.1	0.066	<>									2
3	21.221	4.1834	2	16	7.1	4	4.7	0.170	<>									3
4	22.574	3.9355	4	16	6.0	2	2.4	0.076	<>									4
5	24.360	3.6479	3	222	99.1	53	73.7	0.190	<>	BaB2O4	3.6160	40				24.565	0.205	5
6	25.136	3.5397	4	224	100.0	72	100.0	0.256	<>	BaB2O4	3.5130	100				25.332	0.194	6
7	26.256	3.1555	6	63	26.1	12	15.6	0.143	<>	BaB2O4	3.1310	16				26.464	0.228	7
8	26.943	3.0624	6	49	21.9	12	16.5	0.194	<>									8
9	30.261	2.9511	2	32	14.3	6	10.0	0.179	<>									9
10	32.663	2.7377	3	16	6.0	3	4.0	0.129	<>									10
11	35.361	2.5349	3	76	34.6	36	49.3	0.363	<>	BaB2O4	2.5190	37				35.611	0.231	11
12	37.759	2.3805	2	67	29.9	13	17.4	0.149	<>	BaB2O4	2.3659	11				38.001	0.242	12
13	38.561	2.3326	3	16	7.1	2	2.6	0.100	<>									13
14	42.303	2.1347	5	17	7.6	5	6.4	0.216	<>									14
15	43.062	2.0979	7	32	14.3	8	10.6	0.169	<>									15
16	43.441	2.0814	7	76	33.9	41	56.1	0.424	<>	BaB2O4	2.0660	6				43.297	-0.144	16
17	44.461	2.0351	6	35	15.6	6	7.6	0.124	<>	BaB2O4	2.0239	7				44.741	0.280	17
18	46.359	1.9570	3	17	7.6	2	2.3	0.079	<>	BaB2O4	1.9569	6				46.310	-0.049	18
19	49.256	1.8483	5	17	7.6	4	4.7	0.160	<>									19
20	49.596	1.8365	4	26	11.6	9	12.2	0.270	<>	BaB2O4	1.8300	24				49.765	0.167	20
21	51.461	1.7736	5	19	8.5	1	1.2	0.037	<>									21
22	56.941	1.6156	4	16	6.0	3	3.3	0.106	<>									22
23	67.697	1.3829	7	16	6.0	2	2.3	0.072	<>	BaB2O4	1.3794	17				67.693	0.195	23
24	68.499	1.3667	7	19	8.5	2	2.0	0.061	<>									24
25	71.224	1.3226	2	14	6.3	3	4.1	0.166	<>									25
26	73.061	1.2937	2	14	6.3	2	1.4	0.059	<>									26
@	End-of-List															Average Delta 2-Theta = 0.193		
	> PDF#36-0722 ---------- BaB2O4 - Barium Borate																	

forms β–BBO at 650 °C according to published results [11]. In an attempt to verify those results it was found that the transition is closer to 750 °C. Either way, it has been shown that the replacement of 2-ethoxyethanol by crown ether has decreased the transition by at least 100 °C in the powder form.

3.4 X-Ray Diffraction of Thin Films Formed from Barium Dimesitylborinate Precursor

X-ray diffraction was performed on thin films deposited by spin coating a barium dimesitylborinate solution on silicon wafers and heating them for various times and temperatures. Samples were heated for 1 hour at 500, 550, 600, 650, and 700 °C. The diffraction patterns obtained showed that barium carbonate formed at 500 and 550 °C. At 600 °C crystalline components could not be identified. At the higher temperatures, 650 and 700 °C, barium silicate was identified. The diffraction patterns can be seen in Figures 47 through 51. Films of β–BBO were not identified in any of these cases. It may be possible that boron in the precursor diffuses into the substrate at low temperatures due to high surface energy at the interface. It is also possible that boron oxide forms during heating and sublimes at approximately 450 °C [7]. At the higher temperatures there is definitely interaction with the substrate as determined by the presence of barium silicate.

Another set of wafers was heated at 850 °C for 1, 5, 10, and 30 minutes. In each of these cases barium silicate formed as the only crystalline phase as determined by x-ray diffraction (Figures 52 through 55). The presence of barium silicate indicates substrate interaction at this temperature.

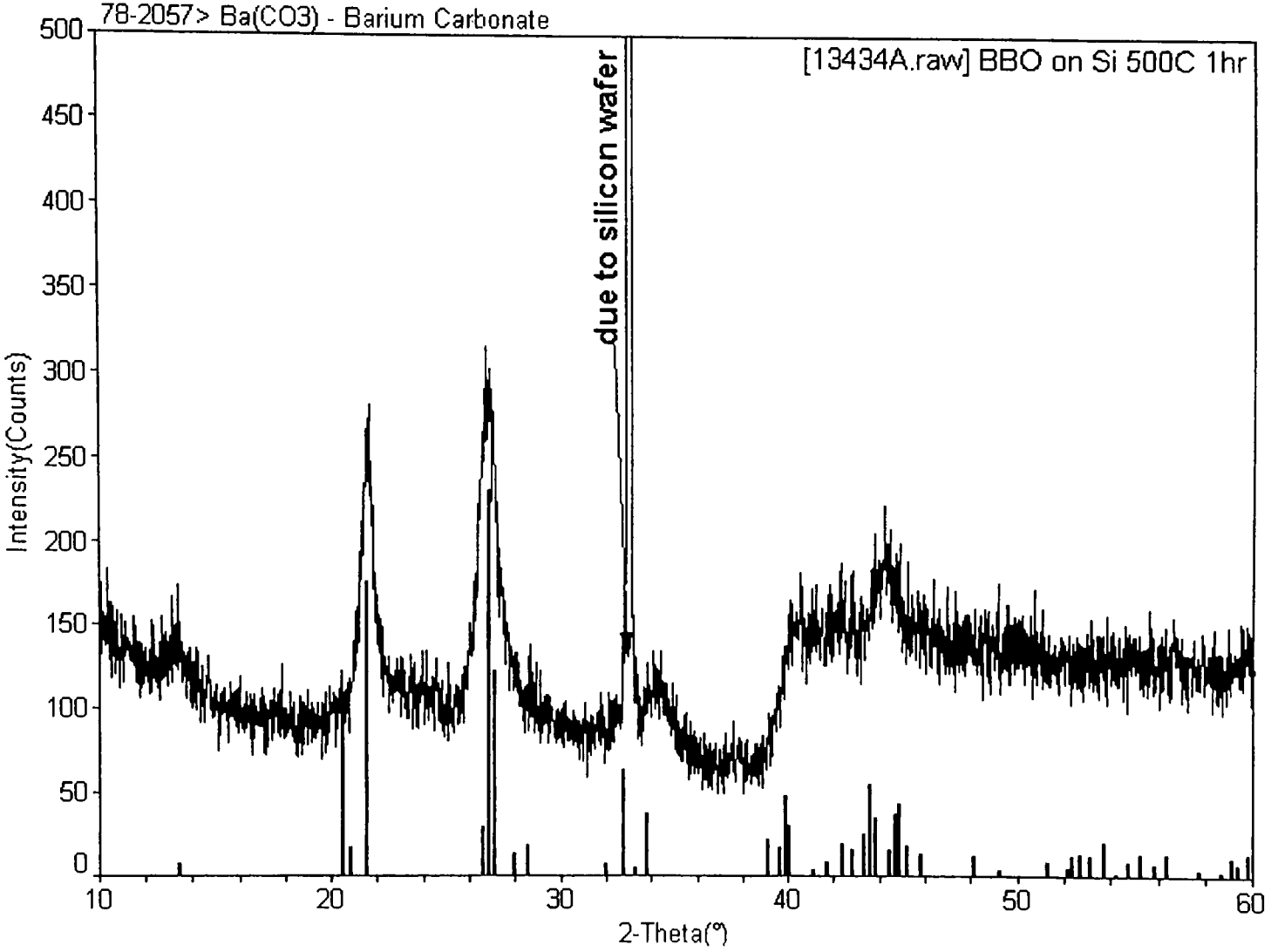


Figure 47. X-Ray Diffraction Pattern for Thin Film of Barium Dimesitylborinate on Silicon Heated to 500 °C for 1 Hour

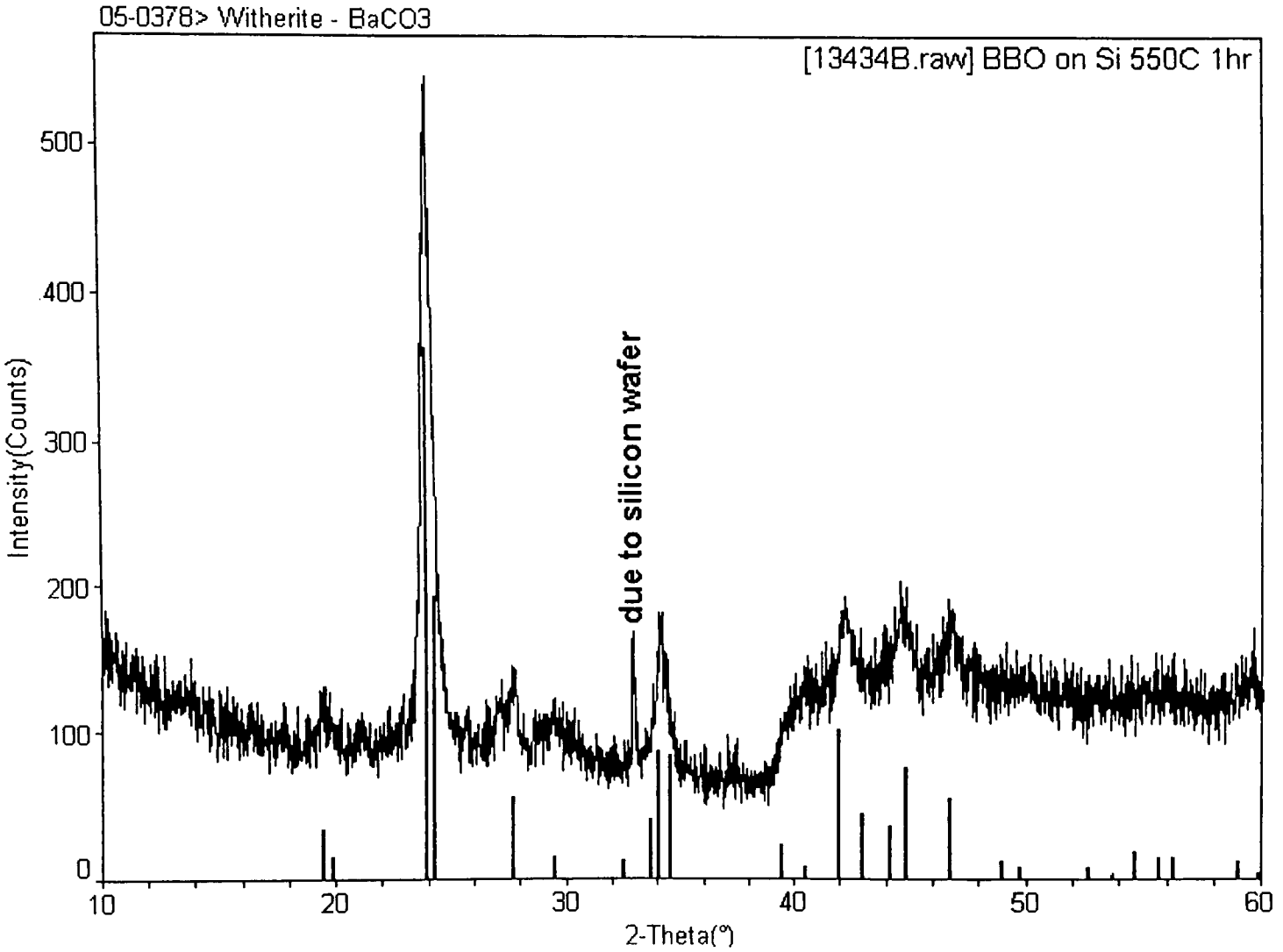


Figure 48. X-Ray Diffraction Pattern for Thin Film of Barium Dimesitylborinate on Silicon Heated to 550 °C for 1 Hour

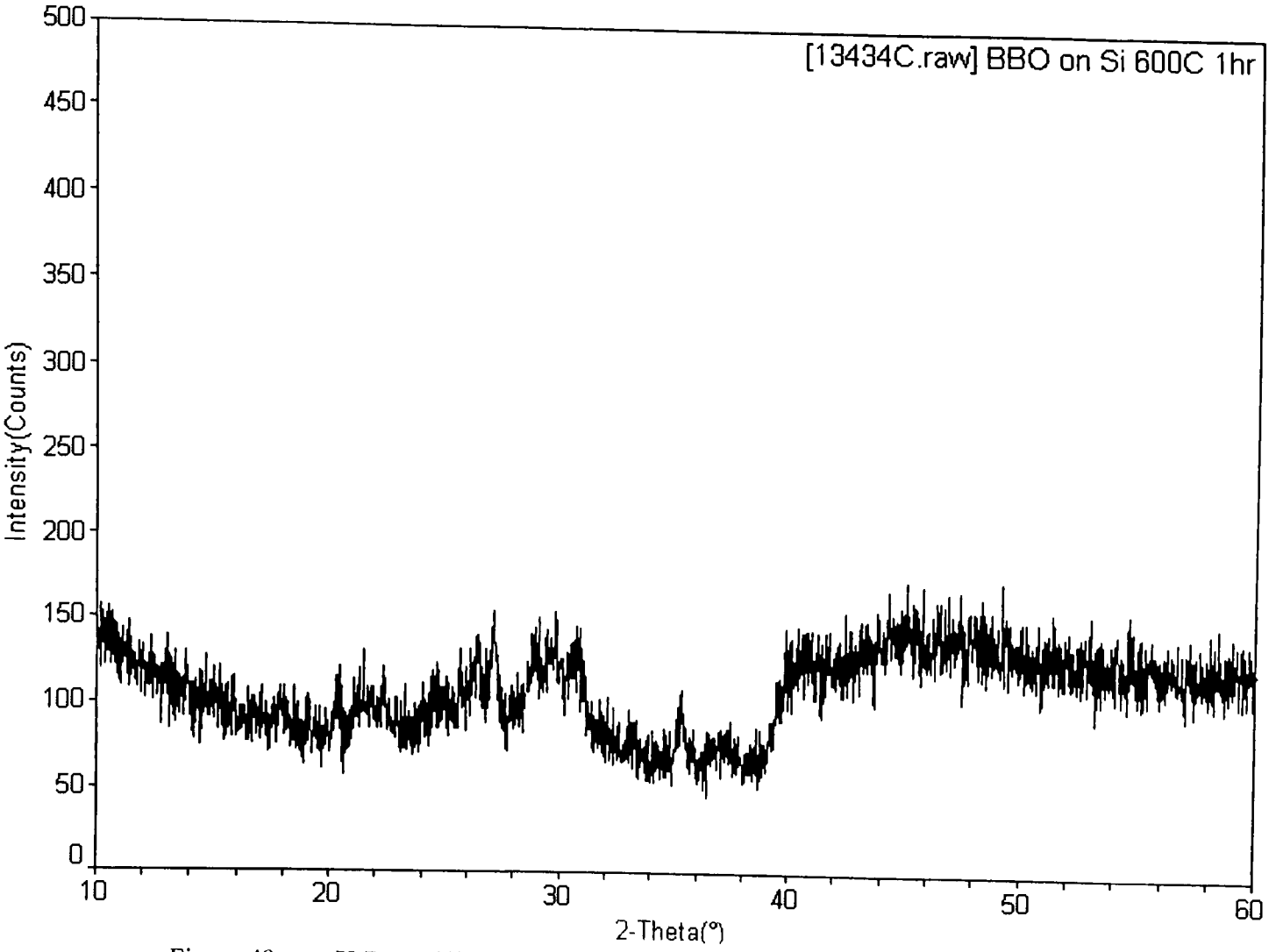


Figure 49. X-Ray Diffraction Pattern for Thin Film of Barium Dimesitylborinate on Silicon Heated to 600 °C for 1 Hour

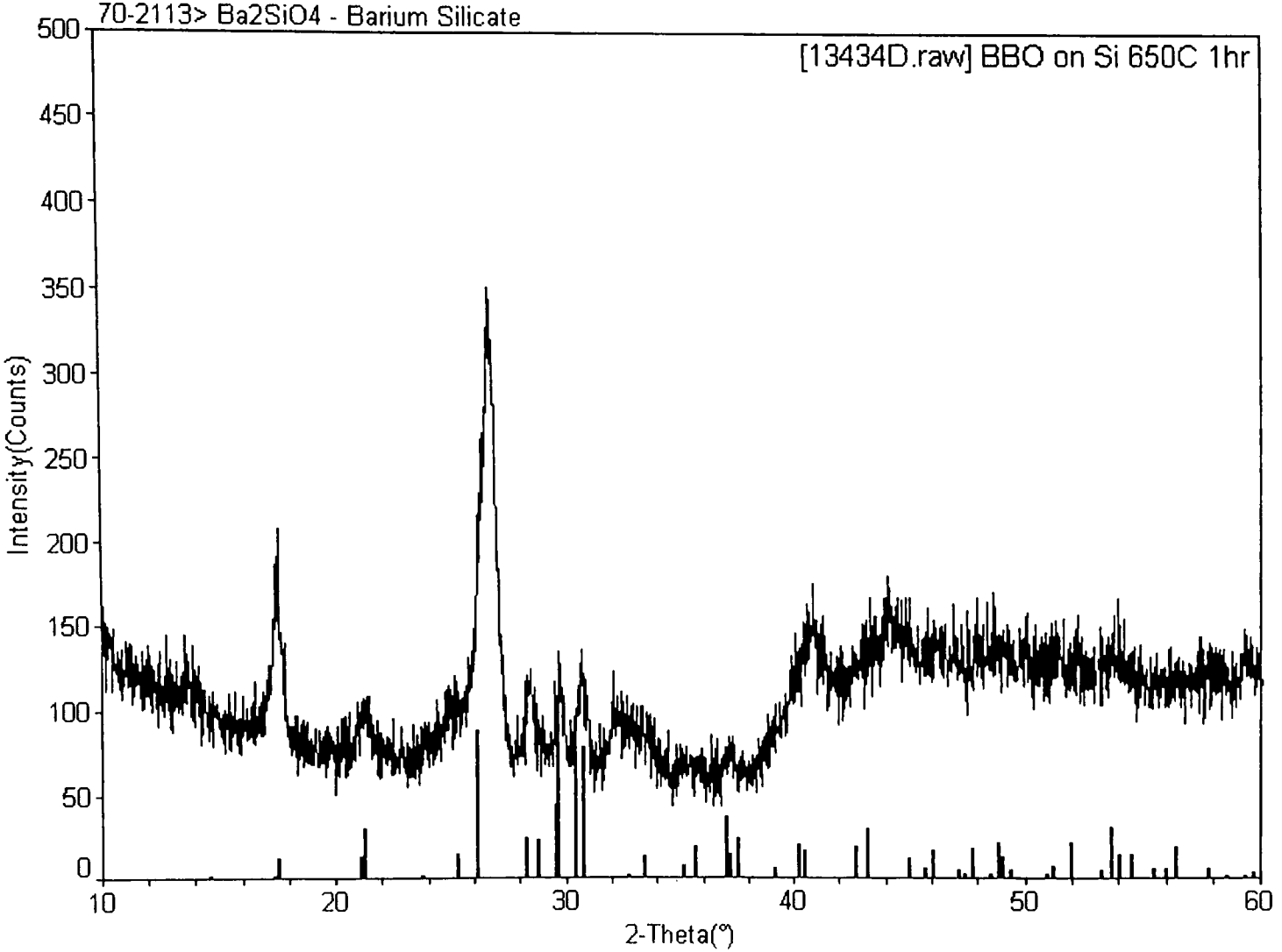


Figure 50. X-Ray Diffraction Pattern for Thin Film of Barium Dimesitylborinate on Silicon Heated to 650 °C for 1 Hour

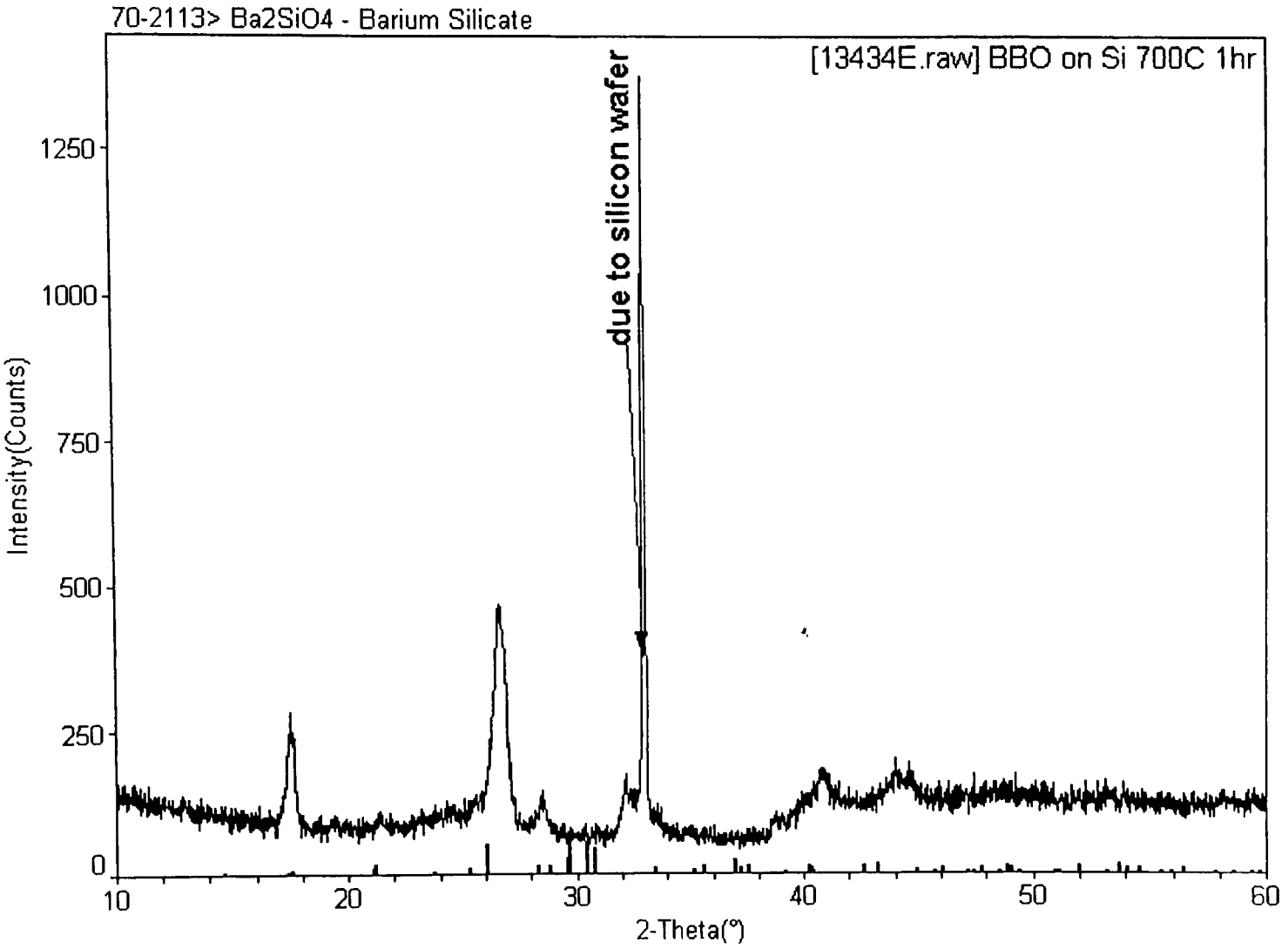


Figure 51. X-Ray Diffraction Pattern for Thin Film of Barium Dimesitylborinate on Silicon Heated to 700 °C for 1 Hour

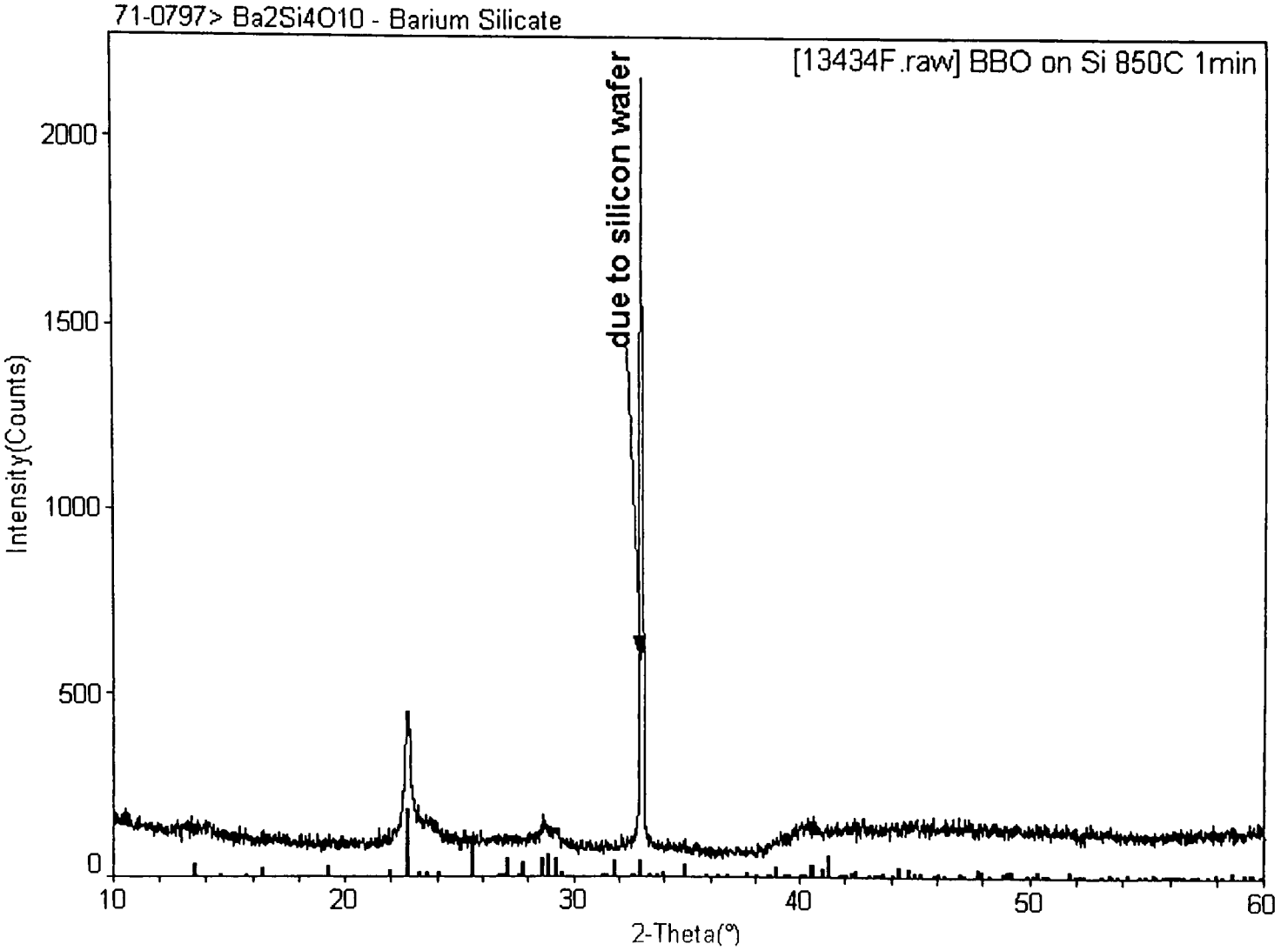


Figure 52. X-Ray Diffraction Pattern for Thin Film of Barium Dimesitylborinate on Silicon Heated to 850 °C for 1 Minute

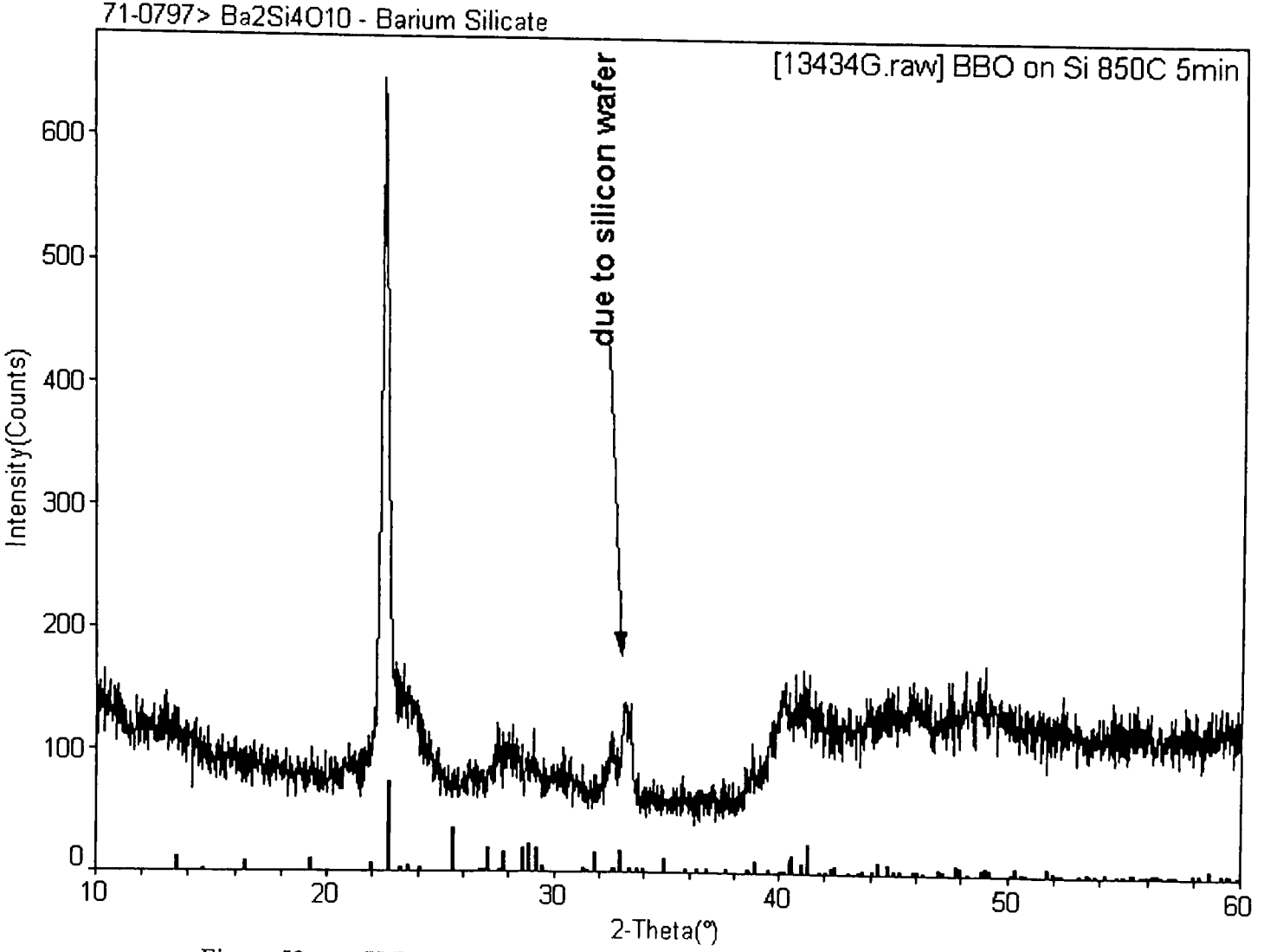


Figure 53. X-Ray Diffraction Pattern for Thin Film of Barium Dimesitylborinate on Silicon Heated to 850 °C for 5 Minutes

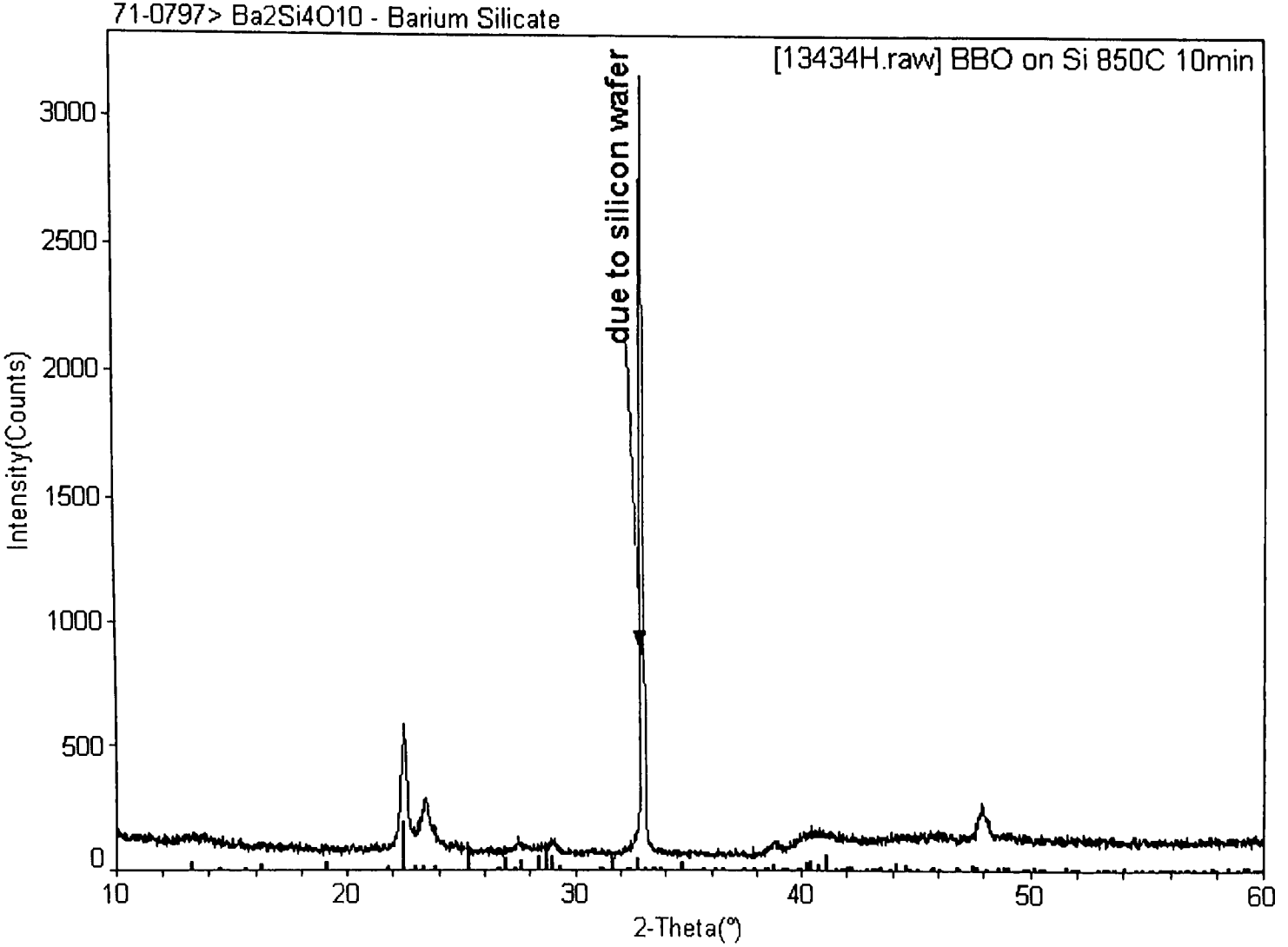


Figure 54. X-Ray Diffraction Pattern for Thin Film of Barium Dimesitylborinate on Silicon Heated to 850 °C for 10 Minutes

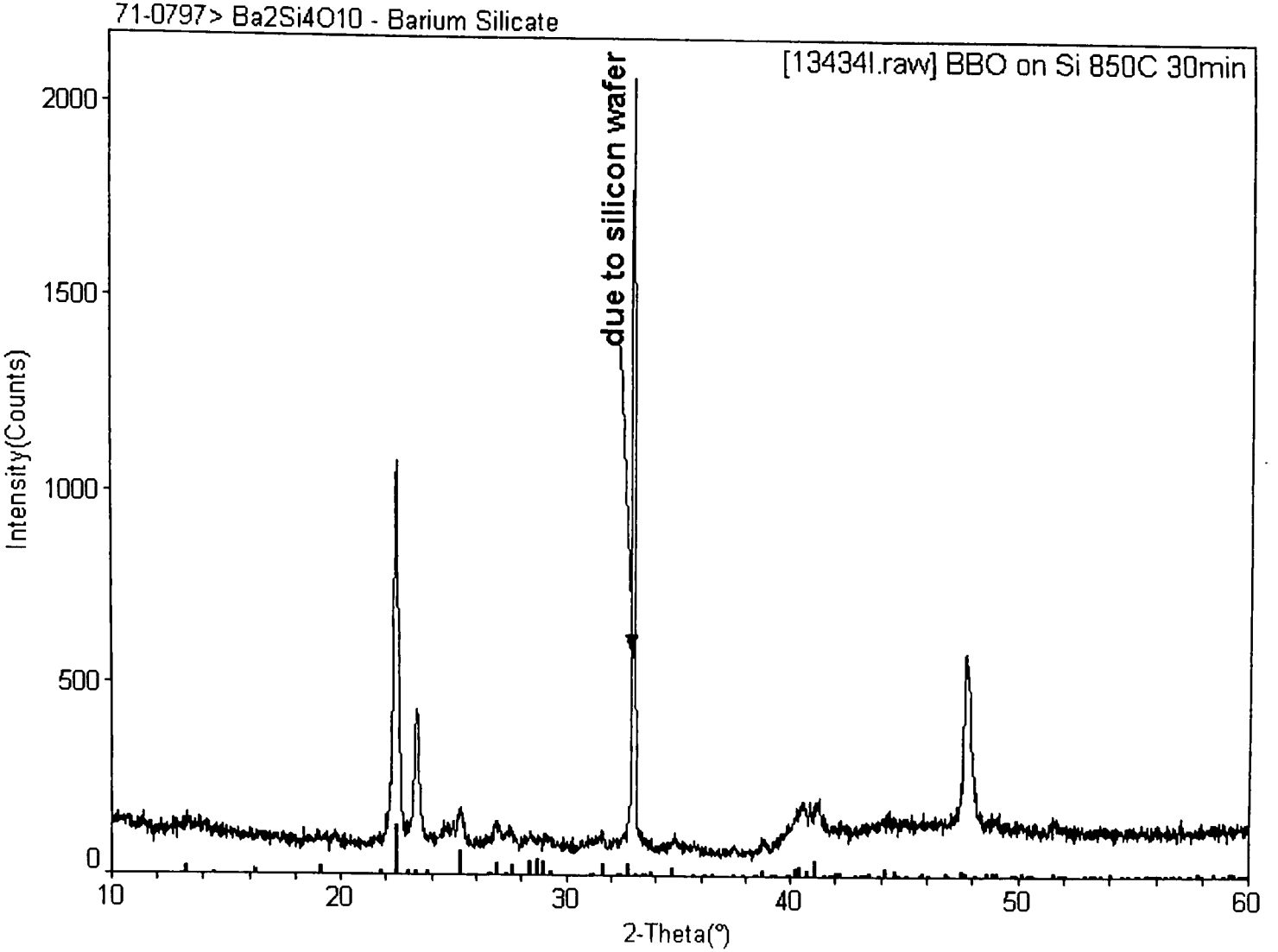


Figure 55. X-Ray Diffraction Pattern for Thin Film of Barium Dimesitylborinate on Silicon Heated to 850 °C for 30 Minutes

Silicon appears to be a poor choice of substrate when trying to form β–BBO thin film for barium dimesitylborinate precursors. A substrate that will be less reactive with the film should be chosen for further experiments.

3.5 X-Ray Diffraction of Thin Films formed from Barium (Crown Ether) Cyclotriboroxane Precursor

X-ray diffraction was also performed on thin films prepared from the barium (crown ether) cyclotriboroxane precursor. The same experimental procedure was used as with the barium dimesitylborinate precursor. Again, five samples were heated for 1 hour at 500, 550, 600, 650, and 700 °C. The X-ray diffraction spectra for these samples are seen in Figures 56 through 60. The samples heated at 500 and 550 °C did not contain any crystalline components. However, β–BBO was determined to be present in films heated to 600, 650, and 700 °C. Another set of diffraction patterns are given in Figures 61 through 64. These samples were heated at 850 °C for 1, 5, 10, and 30 minutes. Crystalline components were not found in any of these samples. If substrate interaction did take place at 850 °C, as for the barium dimesitylborinate precursor, the resulting films were amorphous unlike the crystalline barium silicate obtained previously.

The presence of the six membered ring [4] in the precursor allows β–BBO film formation without any indication of unwanted silicon substrate interaction at temperatures up to 700 °C. The successful growth of films on silicon reflects a potential for integration of β–BBO in silicon based devices. Since the precursor powder formed β–BBO at 550 °C, it was expected that the film should form at even lower temperatures.

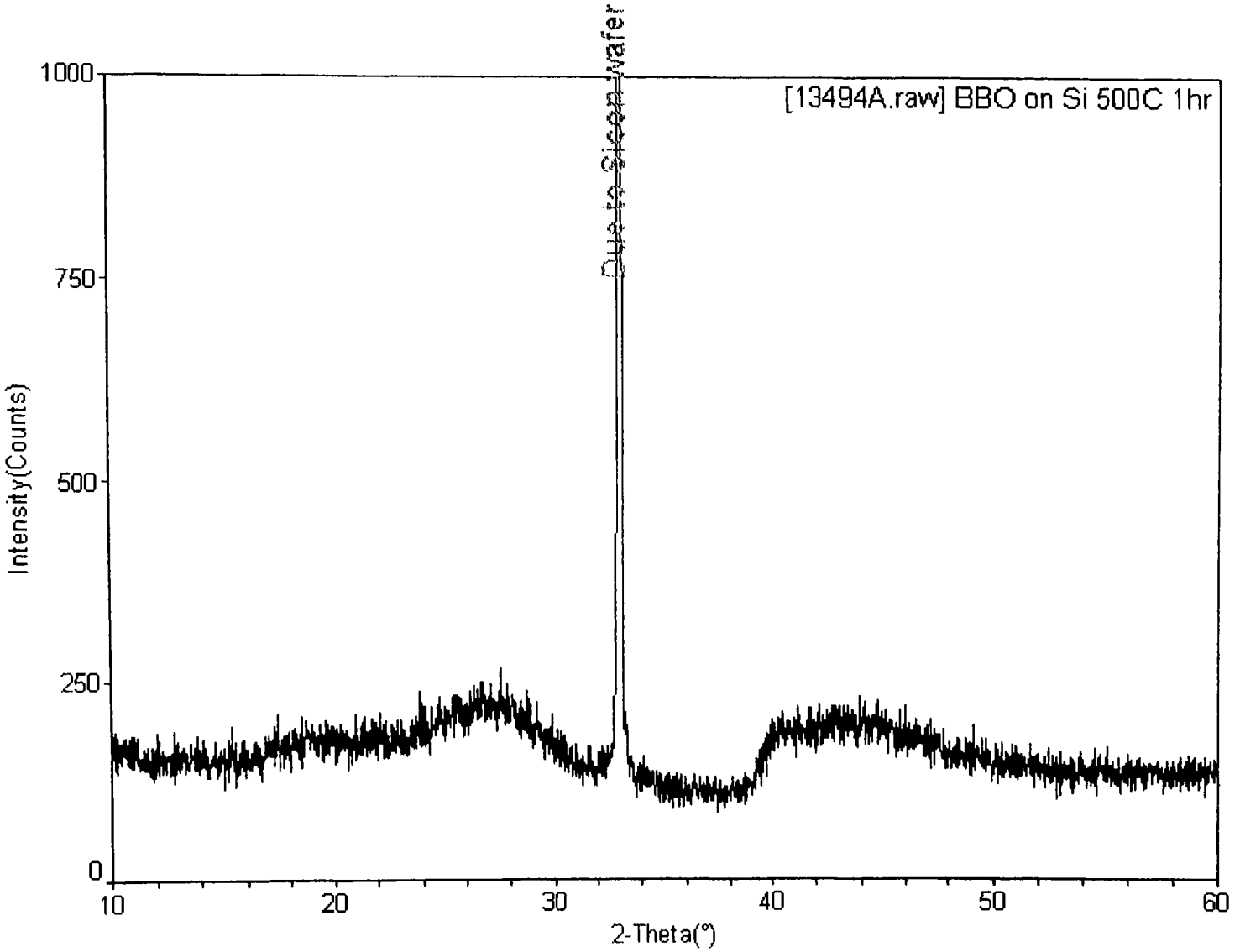


Figure 56. X-Ray Diffraction Pattern for Thin Film of Barium (Crown Ether) Cyclotriboroxane on Silicon Heated to 500 °C for 1 Hour

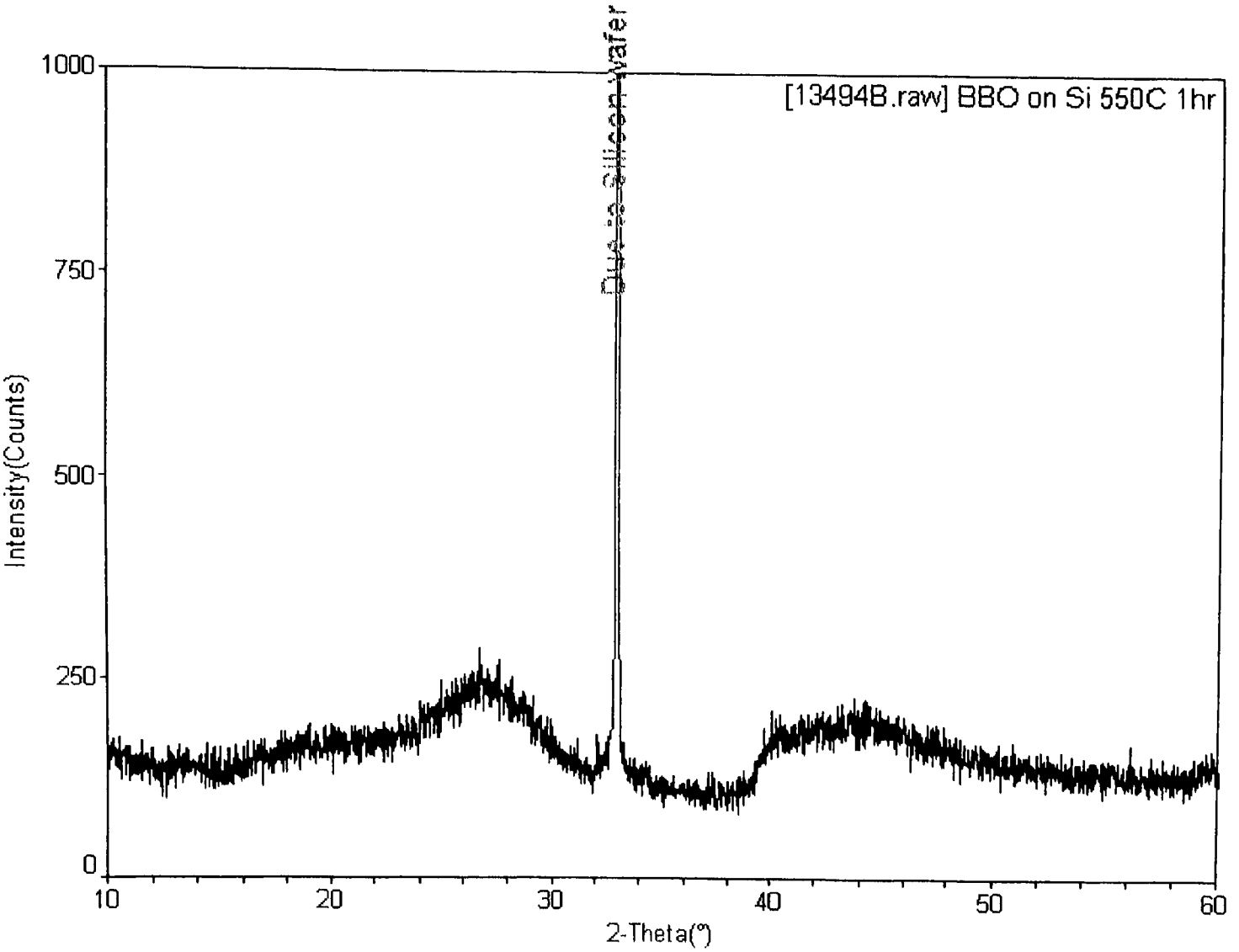


Figure 57. X-Ray Diffraction Pattern for Thin Film of Barium (Crown Ether) Cyclotriboroxane on Silicon Heated to 550 °C for 1 Hour

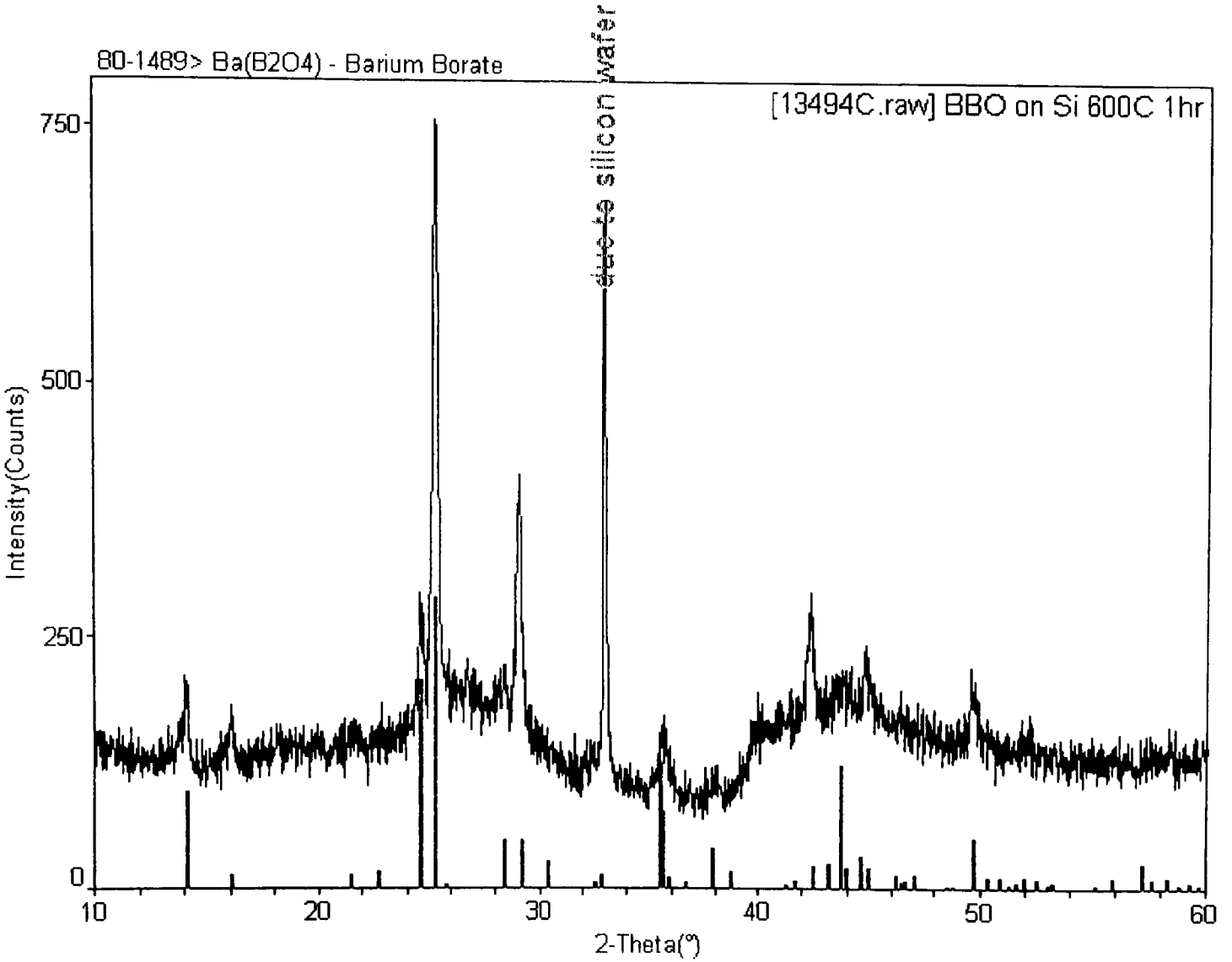


Figure 58. X-Ray Diffraction Pattern for Thin Film of Barium (Crown Ether) Cyclotriboroxane on Silicon Heated to 600 °C for 1 Hour

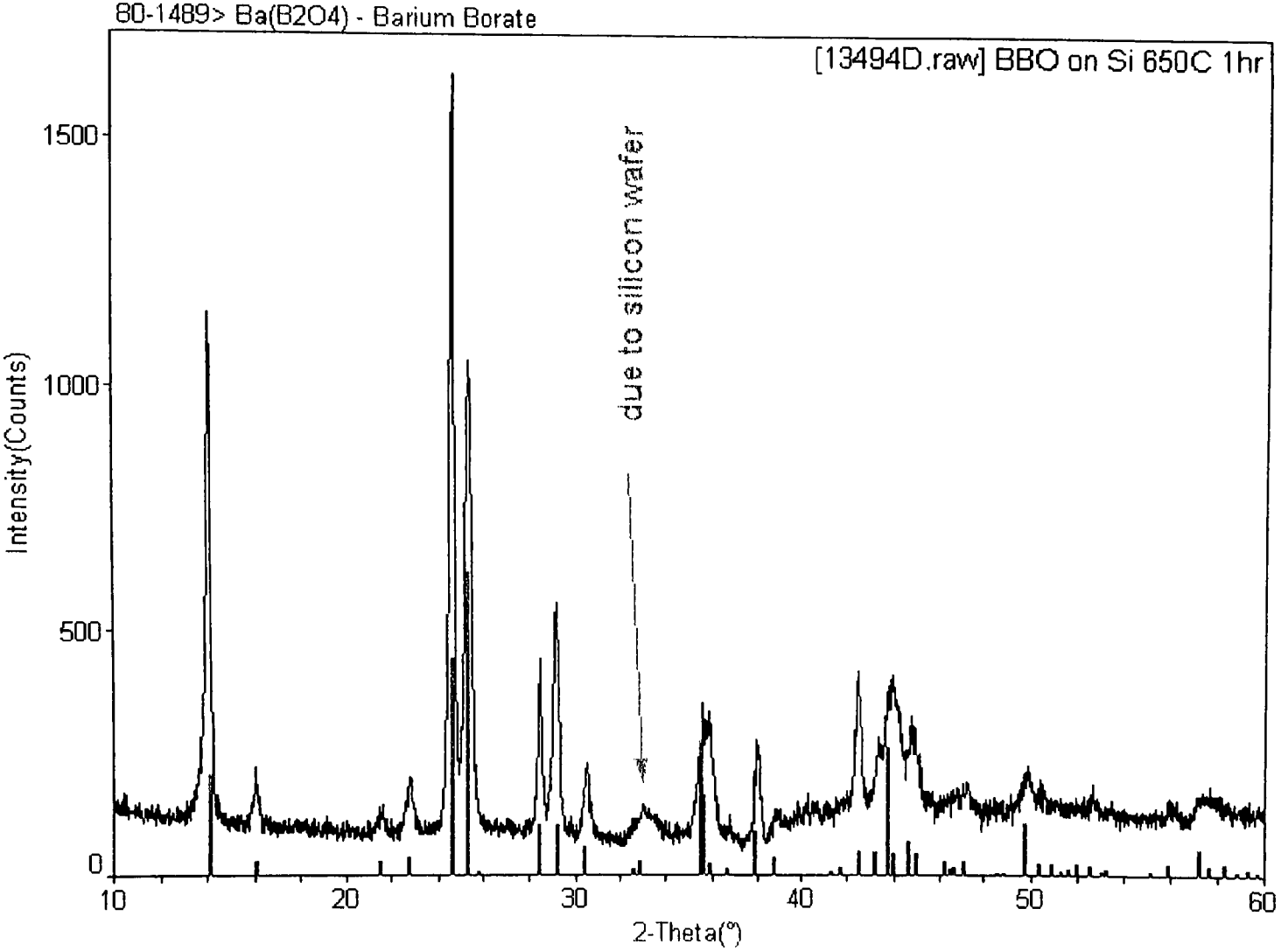


Figure 59. X-Ray Diffraction Pattern for Thin Film of Barium (Crown Ether) Cyclotriboroxane on Silicon Heated to 650 °C for 1 Hour

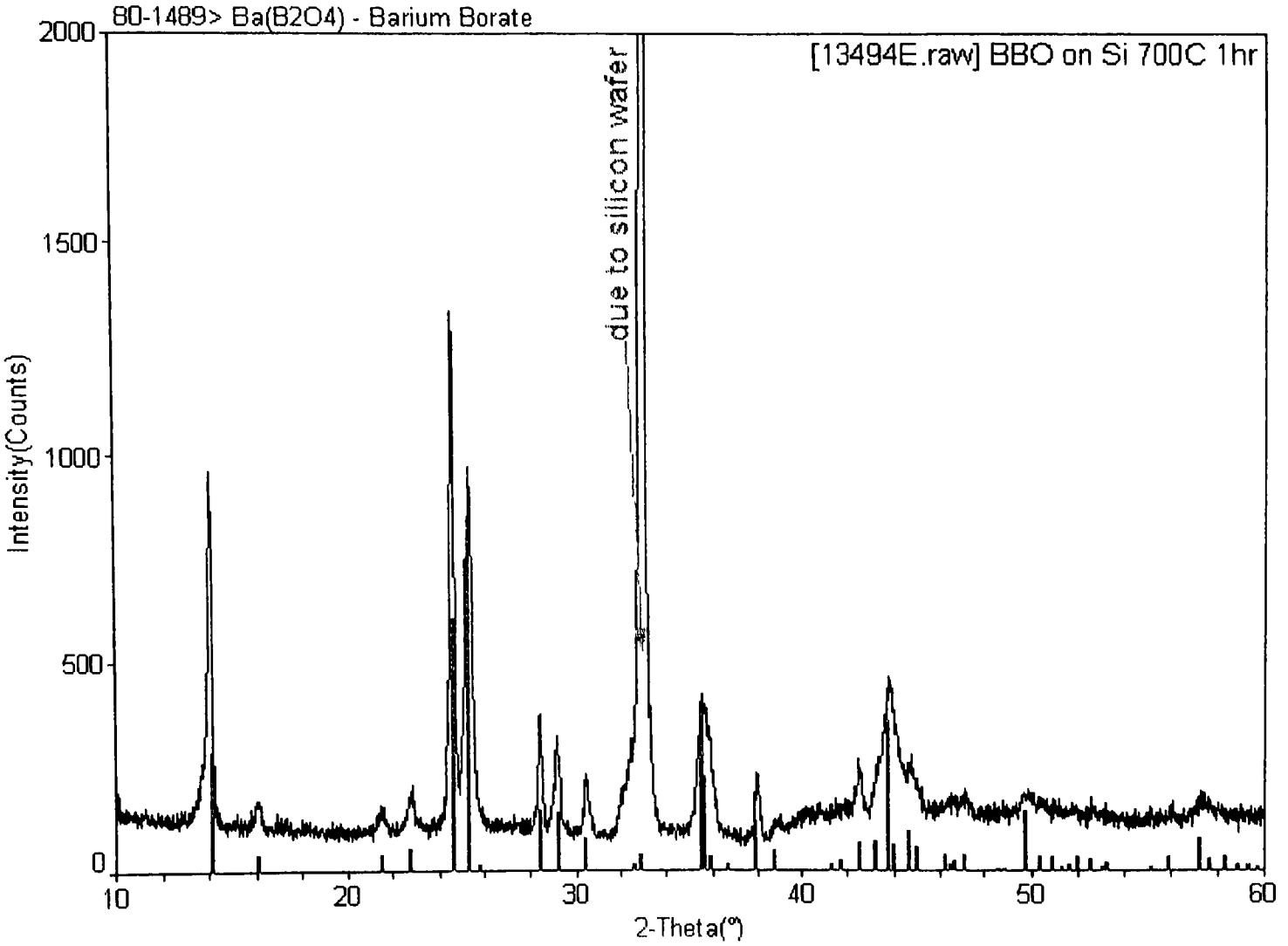


Figure 60. X-Ray Diffraction Pattern for Thin Film of Barium (Crown Ether) Cyclotriboroxane on Silicon Heated to 700 °C for 1 Hour

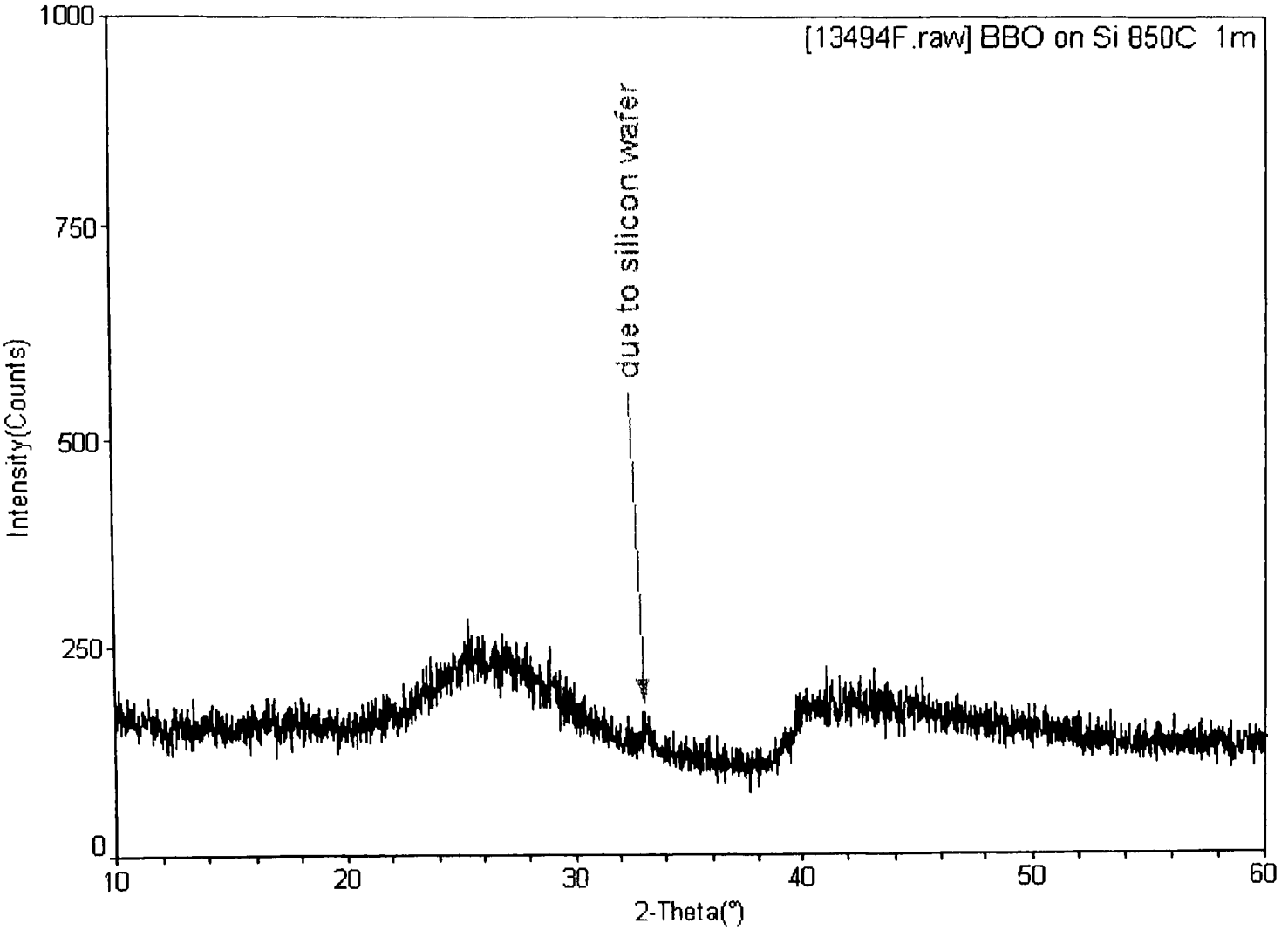


Figure 61. X-Ray Diffraction Pattern for Thin Film of Barium (Crown Ether) Cyclotriboroxane on Silicon Heated to 850 °C for 1 Minute

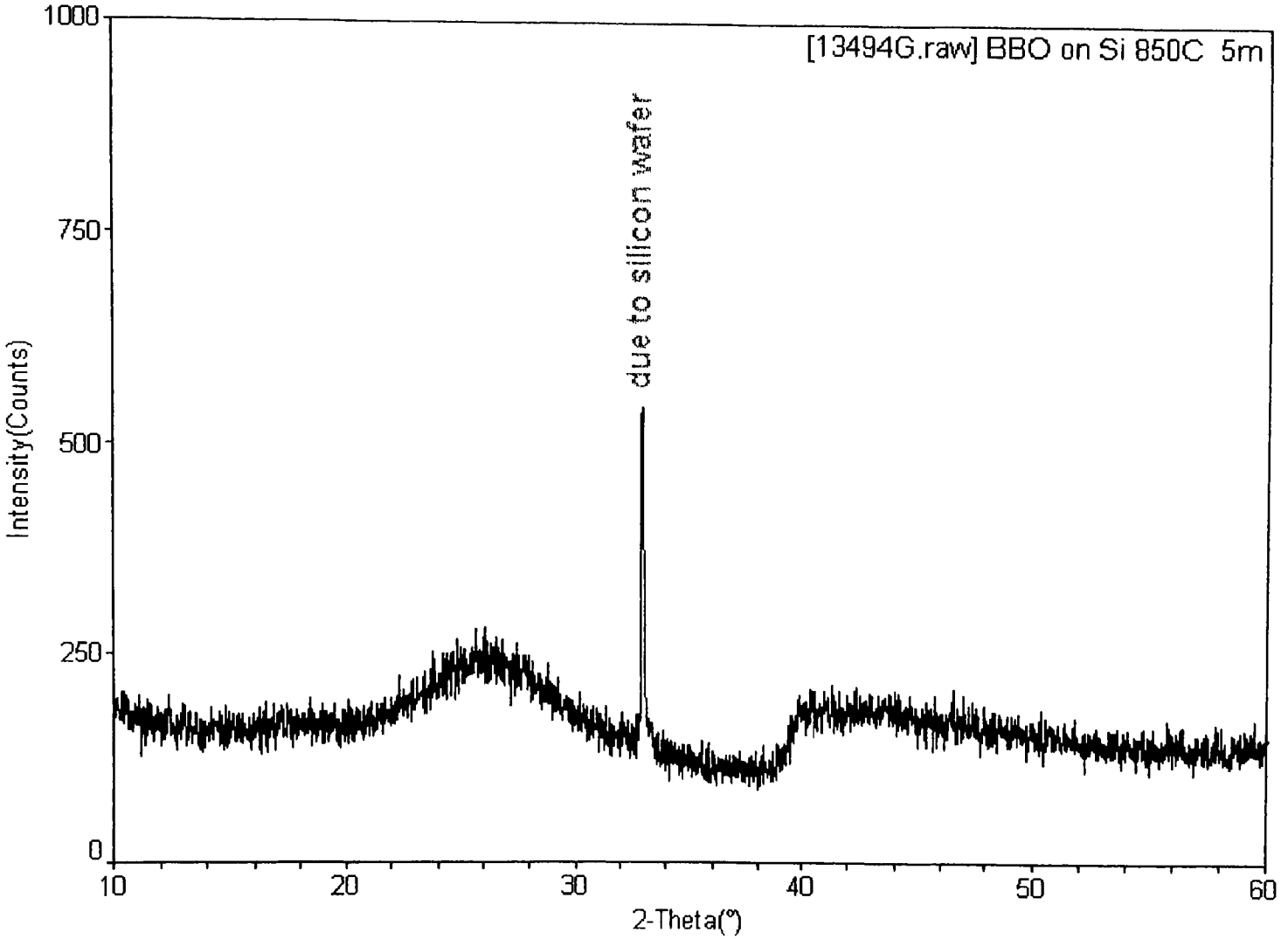


Figure 62. X-Ray Diffraction Pattern for Thin Film of Barium (Crown Ether) Cyclotriboroxane on Silicon Heated to 850 °C for 5 Minutes

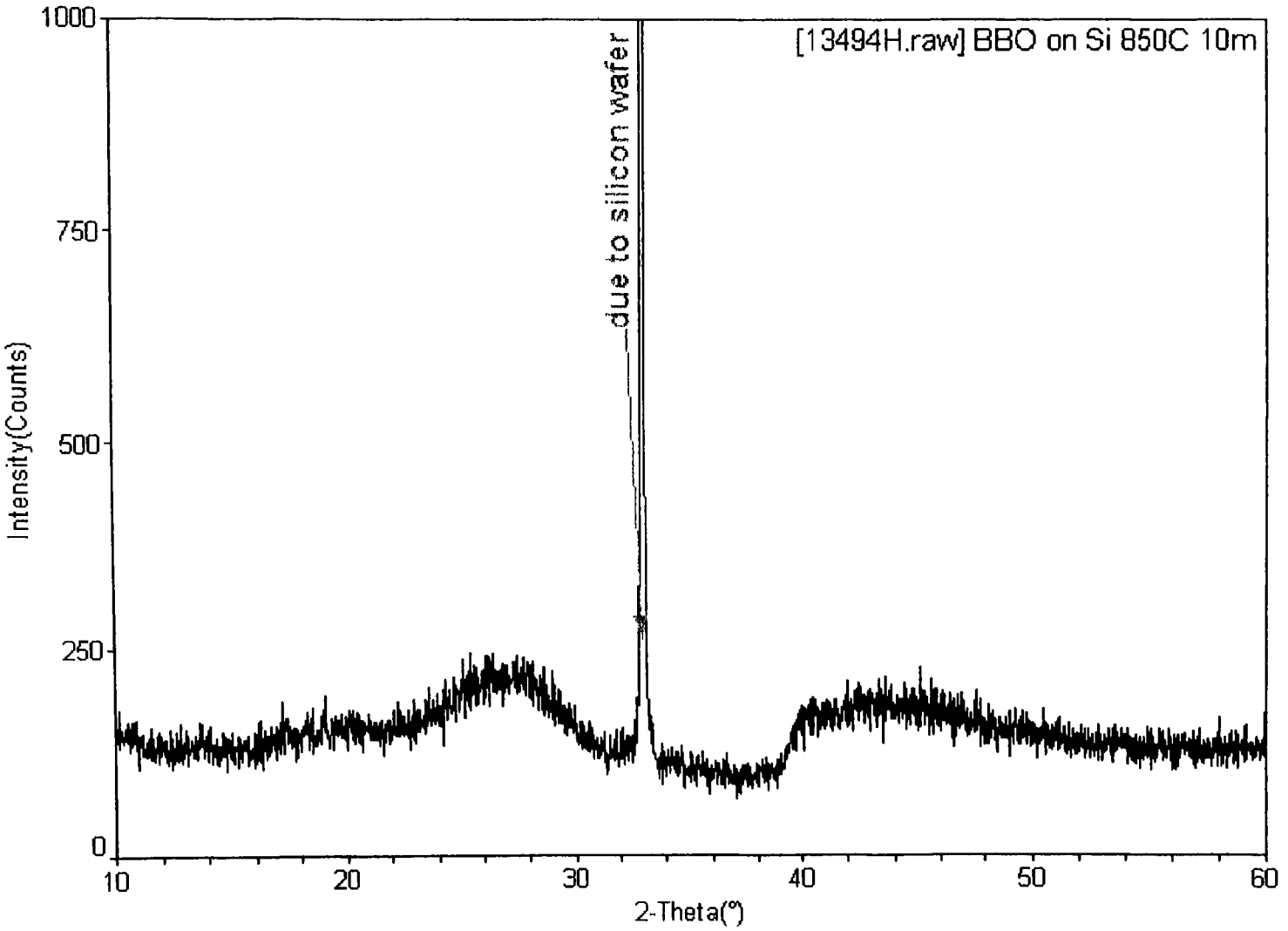


Figure 63. X-Ray Diffraction Pattern for Thin Film of Barium (Crown Ether) Cyclotriboroxane on Silicon Heated to 850 °C for 10 Minutes

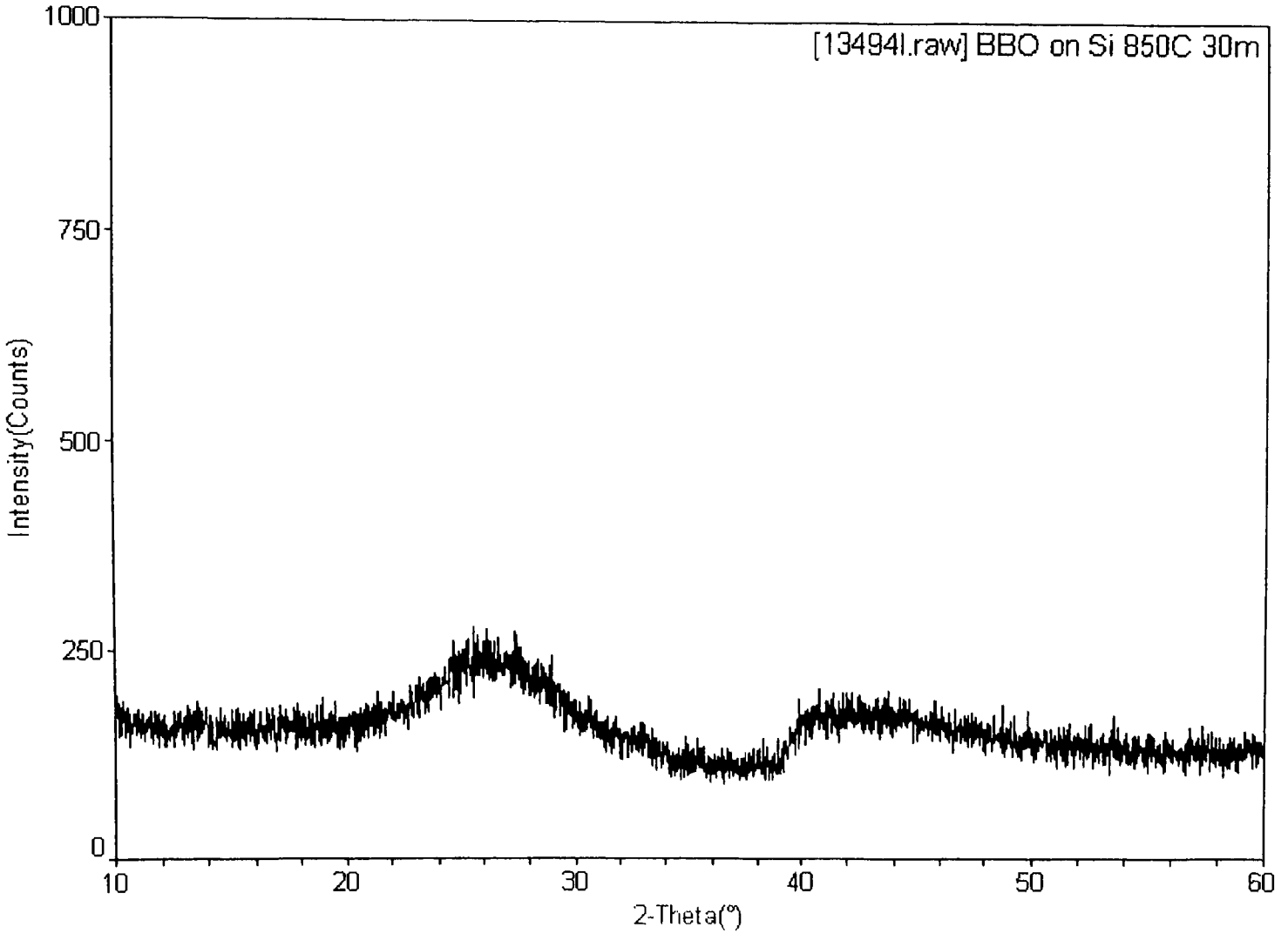


Figure 64. X-Ray Diffraction Pattern for Thin Film of Barium (Crown Ether) Cyclotriboroxane on Silicon Heated to 850 °C for 30 Minutes

This behavior was observed by Yogo when comparing the powder and film transitions for his precursor, although Yogo used platinum rather than silicon substrates [11]. Lower transition temperatures may be obtained through the use of other substrates.

An updated PDF file (80-1489) was used to identify β–BBO when using the thin film X-ray diffractometer and its accompanying software.

3.6 Ellipsometry

Ellipsometry was performed on thin film samples prepared from barium dimesitylborinate and barium (crown ether) cyclotriboroxane precursor solutions. Two of three unknowns (real index of refraction, imaginary part of index of refraction, and thickness) may be simultaneously determined by this method. Samples of both precursors were heated for 1 hour at 650 °C and measured. Tables XI, XII, and XIII give the ellipsometry data taken for a transparent thin film prepared from barium dimesitylborinate. For transparent films the index of refraction and thickness can be determined simultaneously. These values are found when the imaginary part of the index of refraction, k, is zero. The column labeled error is the value of k on the data sheets. At the point where the error column goes through zero the index of refraction and thickness are determined. The index of refraction for this sample was determined to be 1.51. Possible film thicknesses include 542.8, 2840.9, 5139, 7427.1, 9735.2, 12033.3, 14331.4, and 16629.5 Angstroms. Tables XIV, XV, and XVI give the results for the thin film prepared from barium (crown ether) cyclotriboroxane. Since the film was highly

Table XI. Ellipsometry of Thin Film formed from Barium Dimesitylborinate

BBO/SI MOST TRANSPARENT SAMPLE

NF	1.100	0.400	4.000	0.000	0.000	0.000
NS	4.050	0.000	0.000	0.007	0.000	0.000
CD	358.300	28.100	87.500	151.300	315.000	0.000
CD	358.300	28.100	87.500	151.300	315.000	

DEL1= 86.599976 PSI1= 28.099998

DEL2= 85.000008 PSI2= 28.699997

DEL= 85.789986 PSI= 28.398510

Table XII. Output Data for Ellipsometry of Thin Film formed from Barium Dimesitylborinate

INDEX OF MEDIUM= 1.00000 ANGLE OF INCIDENCE= 70.000 WAVE LENGTH= 5461.0 TC= 1.00000 DELC= 90.000

THICK	NF REAL	KAPPA	ADSORPTION	D DEL	D PSI	ERROR	NF-NM	NS-NF	WT FRACTION	NS REAL	KAPPA	K
1212.0	1.10000	0.00000	2.6959E-03	35.594	-2.969	-664.38751	0.10000	2.95000	0.22243	4.05000	0.00692	2
551.3	1.50000	0.00000	5.5131E-03	0.399	0.110	-4.44048	0.50000	2.55000	1.00000	4.05000	0.00692	2
416.9	1.90000	0.00000	6.5942E-03	-7.167	-3.493	67.15092	0.90000	2.15000	1.58182	4.05000	0.00692	2

Table XIII. Results for Ellipsometry of Thin Film formed from Barium Dimesitylborinate

THICK	NF REAL	KAPPA	ADSORPTION	D DEL	D PSI	ERROR	NF-NM	NS-NF	WT FRACTION	NS REAL	KAPPA	K
542.8	1.51484	0.00000	5.5642E-03	-0.002	0.000	0.01814	0.51484	2.53516	1.02501	4.05000	0.00692	2

THE THICKNESS AT WHICH DEL & PSI REPEATS = 2298.1

OTHER FILM THICKNESSES ARE 2840.9 5139.0 7437.1 9735.2 12033.3 14331.4 16629.5

CONFIDENCE LIMITS OF FILM THICKNESS IS 542.1 TO 543.6

CONFIDENCE LIMITS OF THE REAL PART OF INDEX OF REFRACTION OF FILM IS 1.513
87 TO 1.51563

CNS 0.000 0.000 0.000 0.000 0.000 0.000
INDEX OF SUBSTRATE= 1.4385 1.3065 DEL= 85.790 PSI= 28.399
STOP 0.000 0.000 0.000 0.000 0.000 0.000

Table XIV. Ellipsometry of Thin Film formed from Barium (Crown Ether) Cyclotriboroxane

BBO/SI SAMPLE II

NF	1.100	0.400	4.000	0.000	0.000	0.000
NS	4.050	0.000	0.000	0.007	0.000	0.000
CD	352.000	20.800	83.900	155.100	315.000	0.000
CD	352.000	20.800	83.900	155.100	315.000	

DEL1= 74.000000 PSI1= 20.800003

DEL2= 77.800011 PSI2= 24.899992

DEL= 76.089882 PSI= 22.869761

Tabke XV. Output Data for Ellipsometry of Thin Film formed from Barium (Crown Ether) Cyclotriboroxane

INDEX OF MEDIUM= 1.00000 ANGLE OF INCIDENCE= 70.000 WAVE LENGTH= 5461.00 TC= 1.00000 DELC= 90.000

THICK	NF REAL	KAPPA	ADSORPTION	D DEL	D PSI	ERROR	NF-NM	NS-NF	WT FRACTION	NS REAL	KAPPA	K
981.2	1.10000	0.00000	2.1825E-03	45.733	-0.584	-761.55432	0.10000	2.95000	0.22243	4.05000	0.00692	2
489.6	1.50000	0.00000	4.8961E-03	14.185	3.351	-133.13446	0.50000	2.55000	1.00000	4.05000	0.00692	2
406.6	1.90000	0.00000	6.4317E-03	3.892	1.582	-32.33735	0.90000	2.15000	1.58182	4.05000	0.00692	2
370.9	2.30000	0.00000	7.4204E-03	-3.943	-2.558	34.97042	1.30000	1.75000	2.00082	4.05000	0.00692	2

Table XVI. Results for Ellipsometry of Thin Film formed from Barium (Crown Ether) Cyclotriboroxane

CNDE 0.000 0.000 0.000 0.000 0.000 0.000

INDEX OF MEDIUM= 1.00000 ANGLE OF INCIDENCE= 70.000 WAVE LENGTH= 5461.0 TC= 1.00000 DELC= 90.000

THICK	NF REAL	KAPPA	ADSORPTION	D DEL	D PSI	ERROR	NF-NM	NS-NF	WT FRACTION	NS REAL	KAPPA	K
388.2	2.08242	0.00000	6.9495E-03	0.001	0.000	-0.00800	1.08242	1.96758	1.79027	4.05000	0.00692	2

THE THICKNESS AT WHICH DEL & PSI REPEATS = 1469.3

OTHER FILM THICKNESSES ARE 1857.5 3326.8 4796.1 6265.4 7734.8 9204.1 10673.4

CONFIDENCE LIMITS OF FILM THICKNESS IS 387.9 TO 388.4

CONFIDENCE LIMITS OF THE REAL PART OF INDEX OF REFRACTION OF FILM IS 2.081
25 TO 2.08379

CNS 0.000 0.000 0.000 0.000 0.000 0.000
INDEX OF SUBSTRATE= 1.6874 0.8266 DEL= 76.090 PSI= 22.870
STOP 0.000 0.000 0.000 0.000 0.000 0.000

absorbing (non-transparent) the film may be treated as a substrate. When treating the film in this manner only the real index of refraction and the imaginary part can be determined. The thickness of the film is assumed to be infinity since the underlying substrate does not effect the results. The real part of the index of refraction was found to be 1.68 while the imaginary component was found to be 0.83

A thin film of β–BBO is expected to have an index of refraction in the range of 1.5-1.7. The value for the film prepared from barium dimesitylborinate is in the appropriate range for β–BBO. However, the value obtained for the index of refraction is most likely for a film containing barium silicate as determined by thin film x-ray diffraction. The film prepared from barium (crown ether) cyclotriboroxane gave a slightly higher index of refraction, and the value is in the expected range. In both cases a supplemental technique such as profilometry should be used to determine the correct thickness.

3.6 Optical Microscopy of Thin Films

Optical microscopy was used to obtain 50X magnified images of the thin films prepared from both precursors. Figures 65 and 66 show images of thin films prepared from barium dimesitylborinate and barium (crown ether) cyclotriboroxane precursors, respectively. The image of the barium silicate film prepared by the barium dimesitylborinate precursor has well defined grain boundaries. The amorphous region seen in the image is surrounded by growth fronts from four separate crystallites. The

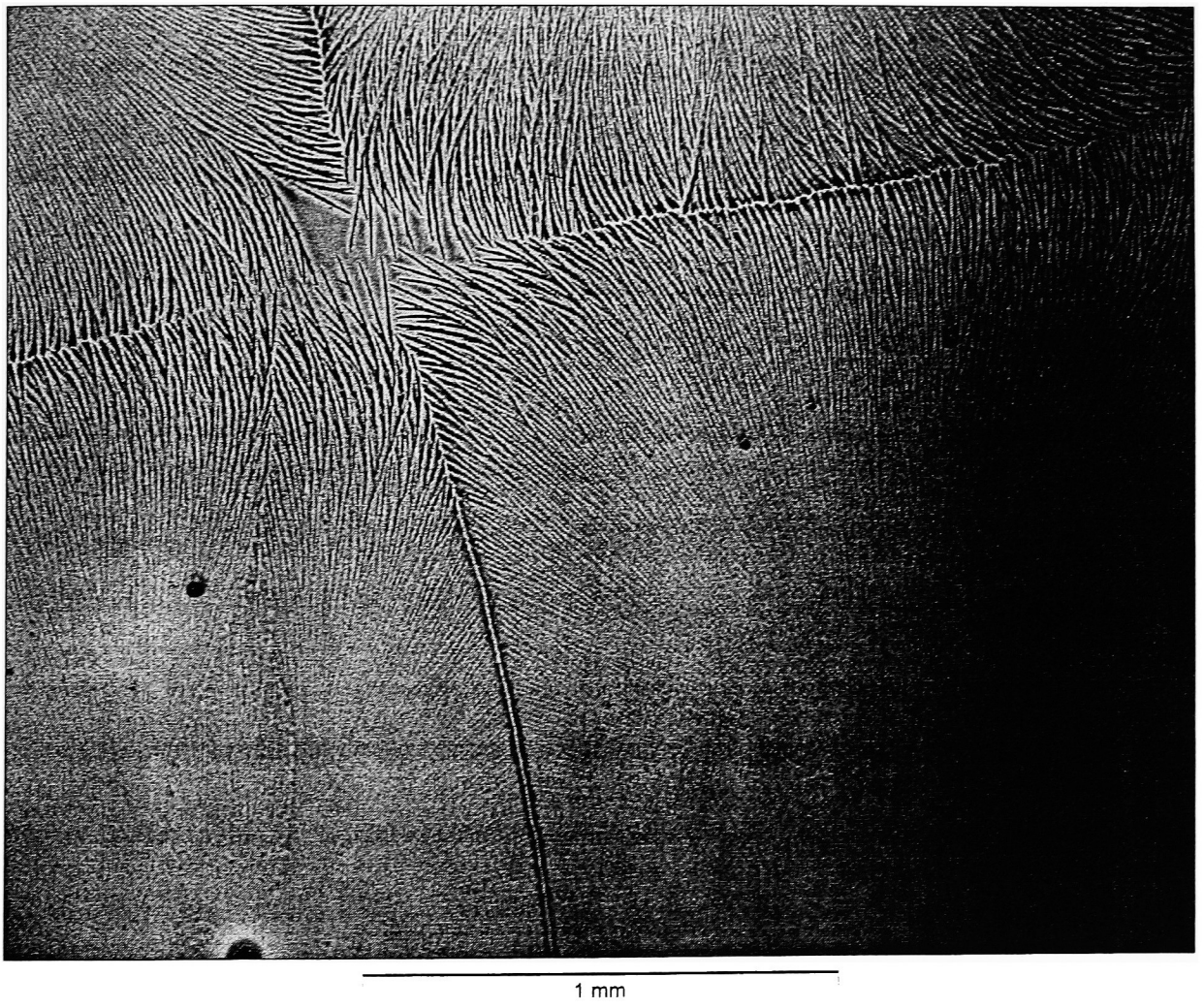


Figure 65. Optical Micrograph of Barium Silicate Thin Film Formed from Barium Dimesitylborinate Heated to 650 °C (50X Magnification)

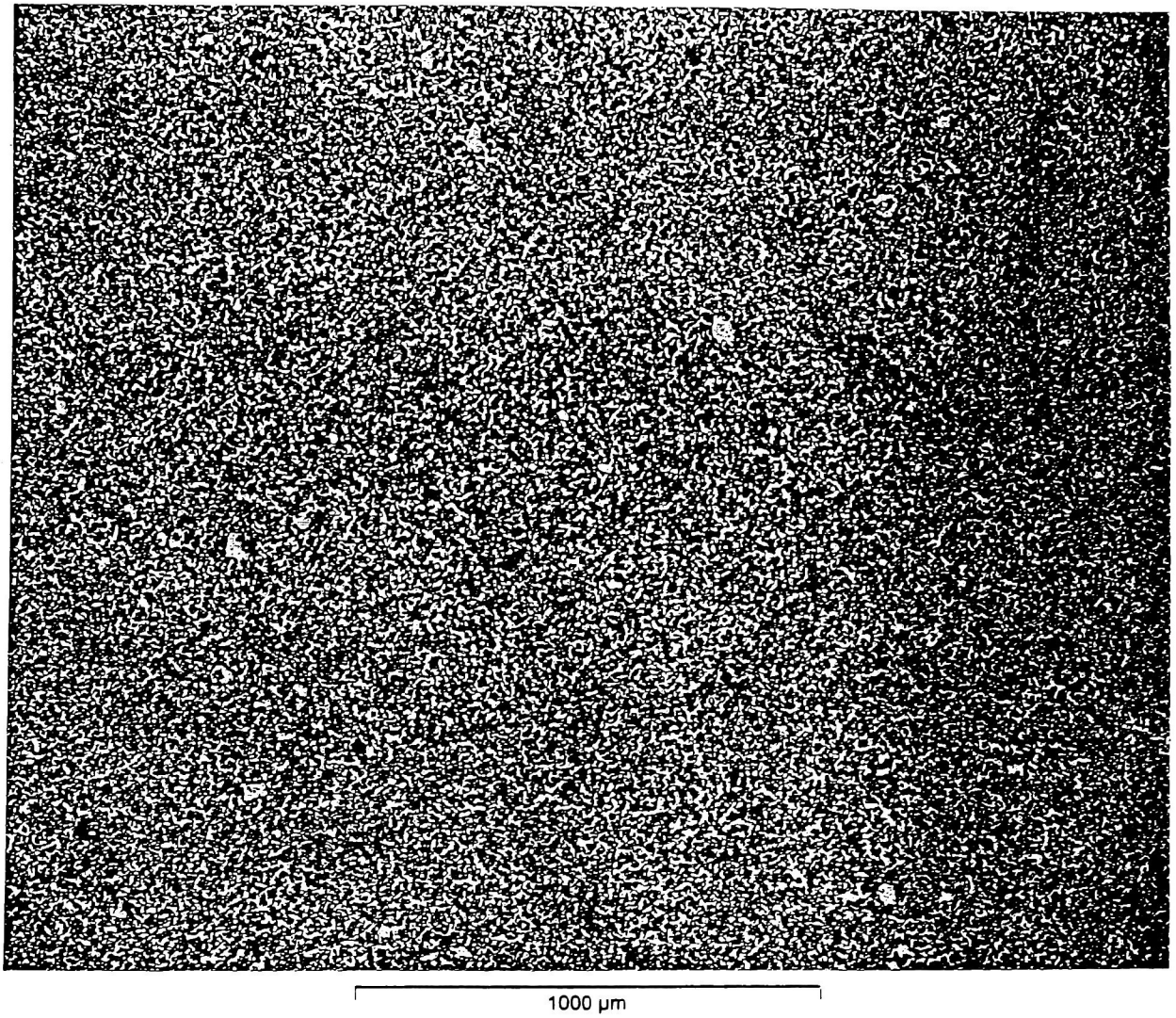


Figure 66. Optical Micrograph of β-BBO Thin Film Formed from Barium (Crown Ether) Cyclotriboroxane Heated to 650 °C (50X Magification)

image of the film prepared by the barium (crown ether) cyclotriboroxane is quite different. This image displays a continuous textured film.

4. SUMMARY

Two novel precursors, barium dimesitylborinate and barium (crown ether) cyclotriboroxane, were synthesized in order to produce thin films of β–barium borate (β–$Ba_3B_6O_{12}$) via the metal organic decomposition (MOD) process.

The formation of β–barium borate was confirmed by powder X-ray diffraction of the products of thermolysis of both precursors. β–barium borate formation occurred at 800 °C and 550 °C for barium dimesitylborinate and barium (crown ether) cyclotriboroxane, respectively. The latter temperature is some 100 °C lower than that which is required to form β–barium borate using the precursor described by Yogo [11].

Thin films were produced by a spin coating precursor solutions on silicon wafers with a (100) orientation. The films were heated to various temperatures for various times then analyzed by thin film X-ray diffraction to determine if β–barium borate was formed. Due to substrate interaction thin films produced from the barium dimesitylborinate precursor did not contain β–barium borate. However, monophasic β–barium borate films were produced from heating the barium (crown ether) cyclotriboroxane precursor to temperatures between 600 and 700 °C for 1 hour.

5. FUTURE WORK

There are many possibilities for future extensions of this research. These include the determination of the optimum substrate for thin films, chemical modifications to the current precursors, improvements to the current product work up, and future characterization techniques.

The most important of these is to find the optimum substrate for epitaxial β–BBO thin film formation. This research has proven that β–BBO has been prepared in the powder form from both barium dimesitylborinate and barium (crown ether) cyclotriboroxane precursors. Due to substrate interactions the same cannot be said of the thin films. Various substrates should be evaluated for the fabrication of high quality β–BBO films. Possibilities include quartz, sapphire, and fused silica to name a few [6-7]. It may also be of interest to deposit films on silicon containing a thick SiO_2 layer [8]. Another possibility is to deposit a very thick film of the precursor on a silicon substrate and attempt to limit the interaction to only the bottom portion of the film.

Chemical modifications could also be made to the novel precursor compounds developed in this research. One possibility is to replace hydrogen atoms from the single source precursor with fluorine atoms in an attempt to volatilize the compound for MOCVD. Another possibility is to add the crown ether to the barium dimesitylborinate single source precursor and examine the change in properties. The addition of crown ether may also help in the isolation of single crystals for x-ray diffraction structural characterization of the precursors.

Improved product work up will result in greater sample purity for elemental analysis and better single crystal growth. The samples to be analyzed by elemental analysis should also be completely dried. Solvents with different boiling points should be used in the Abderhalden apparatus, higher for barium dimesitylborinate and lower for barium (crown ether) cyclotriboroxane. The use of dessicants may also aid in the drying process.

Experimental techniques that will be useful for thin film characterization include glancing angle x-ray diffraction, ellipsometry, profilometry, and scanning electron microscopy. The combination of these techniques will establish the quality of the thin film. Once these techniques have verified a high quality film the next technique to be used is the determination of SHG coefficients using a Nd:YAG laser.

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